ABSTRACT

Title of Thesis: MEASURING AND DEVELOPING A CONTROL STRATEGY FOR ODOROUS GASES FROM SOLIDS HANDLING PROCESSES OF A LARGE WASTEWATER TREATMENT PLANT.

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Odor is the biggest concern and restraint in wastewater and similar industries. A solid-phase microextraction technique was applied to analyze several predetermined odorants. A carboxen-polydimethylsiloxane fiber was used for the analysis of an amine, and several sulfur compounds, and a polyacrylate fiber for the analysis of predetermined volatile fatty acids. Calibration curves were developed within the ranges 0.0004 and 2.9943 ppmv for sulfides and 0.0228 and 2.3309 ppmv for fatty acids and showed R^2 greater than 0.99 . A one year study of the odorants and operation parameters was carried out in a large wastewater treatment plant to develop a correlation between odorants and sludge characteristics to determine factors controlling odor production. Methyl mercaptan and dimethyl sulfide showed highest odor indexes meaning higher human perception. A correlation was found between ORP and sulfides. The DAF thickened sludge and the blended sludge had the highest odor indexes and the lowest ORP's measured.

MEASURING AND DEVELOPING A CONTROL STRATEGY FOR ODOROUS GASES FROM SOLIDS HANDLING PROCESSES AT A LARGE WASTEWATER TREATMENT PLANT

By

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Dedication

I would like to dedicate this thesis to my parents Nelson and Beatriz who have done everything possible for me to have the best opportunities that they could give me. For their guidance and advice that helped me get to where I am today. To my sister for always being there for me, to my brother for always making me laugh, and to Carlos, who I love with all my heart and who always believed in me.

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Chapter 1: Introduction

General Background

Odor is an inescapable problem associated with wastewater treatment operations. Large urban areas require large wastewater treatment plants (WWTPs), and these plants often come under pressure due to public complaints regarding odor emissions. Expanding residential land use in large metropolitan areas like Washington, DC may intrude on the odor "footprint" of a WWTP, necessitating expensive odor control measures to be installed. Especially, solids generated from wastewater processes, or biosolids, can be quite odorous (Kim, 2002). Traditionally, landfilling or incineration was carried out for biosolids disposal, but landfill space has become scarce and incineration is expensive, especially for very large treatment plants. Biosolids application to agricultural fields as a soil conditioner has increasingly been used as an alternative disposal method. For example, the District of Columbia Water and Sewer Authority land-applies biosolids of about 1350 tons/d in Virginia (District, 2002).

Variability in odor intensity associated with the land-applied biosolids can create nuisance odors in residential neighborhoods near the point of application, causing serious pressure from local regulators to limit application to very rural areas. More odorous material has to be taken further from populated areas and is therefore more costly to haul away. In order to produce higher quality biosolids, there is a need to better understand the chemicals and the properties of the sludge responsible for odor problems.

Accurately measuring odorous compounds is challenging due to their volatile and reactive nature. Trained human olfactory panels have been used in the past to provide information on detection thresholds and odor intensity. However, this approach has suffered from variability between panels, and they do not provide compound-specific information. Newly developed electronic nose devices are not sensitive to all compound classes and also do not provide compound-specific information (Francesco, 2001).

Direct chemical analysis of odorants presents several obstacles: 1) development of certified standards over a range of very low concentrations, 2) sample collection without causing analyte transformation or degradation, 3) chromatographic separation of analytes with different polarities (Abalos, 1999). Use of permeation devices to create certified gas standards has been shown to provide acceptable accuracy for these very volatile chemicals (Kim et al., 2001). Solid phase microextraction (SPME) has been utilized successfully in a number of applications for the collection of a wide range of volatiles including odorants from different media (Zeng, 2002). New research shows that it can be used for a wide range of chemical analysis not only in the liquid phase but also in the gas phase over dirty samples (Abalos, 2000).

Gas chromatography coupled with SPME is the analytical technique chosen for this research. Multi-dimensional GC-MS (MD-GC-MS) is a technique that allows pre-separation on a traditional non-polar column followed by further separation on a more polar second column, resulting in improved chromatography especially for polar analytes. This method allows the analyst to analyze samples for multiple compound classes with one instrument.

Project Objectives and Tasks

Improvements in odor analyzing methods are required to monitor and control odorant production within a wastewater treatment system. These improved methods can then be used to test the efficiency of possible odor control strategies. The overall objectives of this research project are to:

1. Evaluate the feasibility of using SPME coupled with MD-GC-MS as a technique to accurately measure odorous compounds.
2. Utilize this technique in a large WWTP setting to measure key odorants from the unit sludge-thickening processes along with ORP and other process parameters, establishing relationship between odorant concentrations and specific process conditions.
3. Evaluate specific oxidants (i.e., potassium permanganate, sodium hypochlorite, potassium ferrate, calcium nitrate) for effectiveness in controlling ORP conditions in sludge and odorant generation for possible use in the plant process for odor control.

Approach to Research Objectives

As part of this work, a methodology to accurately measure key odorants using solid phase microextraction (SPME) coupled to MD-GC-MS was developed. For this study, standard curves were established for the analysis of 15 different compounds that have been found the main odorants coming from wastewater biosolids in the past research. Two different fibers were used: a carboxen polydimethyl-siloxane (Car-PDMS) fiber for the analysis of sulfides, amines and mercaptans, and a polyacrylate fiber volatile fatty acids (VFA's).

After the analytical method was developed, a sampling regimen of weekly samples over one year was carried out at the Blue Plains WWTP, DC to determine which compounds were associated with the different sludge-thickening process and their temporal variability. Sludge was collected from five different points within the plant: a gravity thickener, a dissolved air flotation (DAF) thickener, a blending tank and a centrifuge. The dewatered sludge was then taken to a lab where percent solids were determined and lime was added at 20% by dry mass. Gas in the headspace over each sample was analyzed within 12 hours after collection.

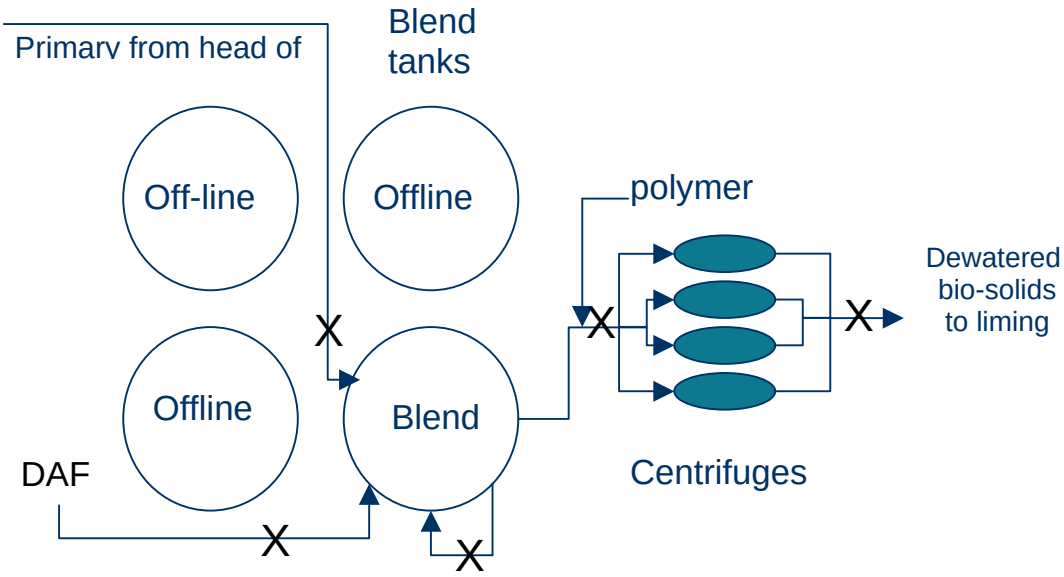


Figure 1.1: Sampling points (X) in the solids processing at Blue Plains Wastewater Treatment Plant.

Other data were also collected on each sampling day, this included iron concentration in the sludge, heterotrophic plate count, calcium, calcium carbonate, flows into and out of each process, level of sludge in storage tanks, amount of polymer added into the centrifuges, flows of sludge into the centrifuge, and centrifuge specs: percent torque, delta RPM, and Amps. The data was used to develop correlations between

oxidation reduction potential (ORP), pH, and other plant conditions in order to use these as predictors and even preventive measures of plant odors.

A separate study using this method was conducted to test the ability of different oxidants to increase ORP and therefore reduce odorant release. Four oxidants were chosen and applied to the sludge in a laboratory setting. These oxidants were sodium hypochlorite, calcium nitrate, potassium ferrate, and potassium permanganate. Three different doses of oxidants were used and ORP was measured at 4 hour intervals for 24 hours. Every time ORP reading was taken, odorous compounds were also quantified to evaluate the correlation between ORP and released odorous compounds.

Relevance and Expected Benefits

Odor control is a very important parameter that must be included into the overall management plan for a WWTP. This research expands on the previous study on odor analysis (Kim *et al.*, 2001), and provides a more efficient, sensitive method. Because of its ease of use, any plant with a lab and a GC-MS system can perform its own odor studies without the need of bringing in an odor panel, and can change operation of unit process to reduce the odor release within a reasonable amount of time. They will also gain information on correlations which were made between odorants and conditions of different unit processes producing biosolids in different times of the year.

Future plans are to use the correlations found in this thesis to install on-line monitoring systems that will allow for quick modifications of plant conditions in order to minimize downstream odors. In this way, the quality of final biosolids product can be improved and overall disposal cost will be lowered.

The oxidation study performed at the end of this thesis is an innovative technique that can begin future research on the addition of chemicals that will decrease the amount of odorants given off, more specifically of reduced sulfurs, by improving the oxidation conditions of sludge. This technique can have an impact on and is of great importance to WWTPs. The technique can be applied on site since it is utilizing a parameter which is easy to measure, ORP, therefore allowing process controllers to make decisions leading to a decrease in downstream odors which could lead to complaints from the public.

Chapter 2: Background

Wastewater Treatment and Odor Control

Wastewater treatment plants (WWTPs) all over the world encounter many challenging tasks. With increased environmental concerns and growing populations, plants must deal with stringent regulations on effluent quality, but also on sludge quality and odor released from the unit processes. Public concerns due to odors dictate where a plant can be built, how much an existing plant can grow, and where resulting biosolids can be disposed. Limited methods for odor analysis and unreliable information on odorant formation and release make odor control a tough challenge to WWTP operators.

Blue Plains Wastewater Treatment Plant

The Blue Plains WWTP, where all the samples for this research were collected, is the largest advanced WWTP in the world, with a treatment capacity of 370 million gallons per day. It is located in Washington D.C. and serves not only the District but also parts of Virginia and Maryland. It treats mainly municipal wastewater but also some industrial. Although some construction is underway to separate sewage lines for wastewater and storm water run-off, influent flows to the plant through combined sewers.

Wastewater entering the plant first goes through grit chambers where the heavy inorganic grit and debris are removed and then to primary sedimentation tanks where about half of the suspended solids settled down. These solids removed in the primary sedimentation tanks are further concentrated in thickeners by gravity. This primary settling process is followed by a secondary step-feed aerated activated sludge process

where most of the organics in wastewater are removed. The treated wastewater then flows into secondary settling tanks where solids and liquid are separated and a portion of the settled solids are re-circulated to the head of the secondary process in order to maintain the microbial population. The rest of the solids are sent to dissolved air flotation (DAF) thickeners. The wastewater that flows out of the secondary settling tanks then goes to nitrification-denitrification tanks. Again excess sludge from nitrification-denitrification processes is sent to the DAF thickeners. The treated wastewater then flows to sand and anthracite filters for the final removal of fine particles and phosphorus. After the filters, the water is disinfected and discharged into the nearby Potomac River.

All the thickened sludge from DAF and gravity thickeners is combined in blending tanks, varying with an optimum ratio of 1 to 1. Outflow of the blending tanks is mixed with polymer, and pumped into solid bowl decanter type centrifuges for dewatering. After centrifugation, the dewatered cake is conveyed to a liming process and placed in storage areas until it is removed, loaded on to trucks, and hauled away for land application. In a preliminary study of odor-causing chemicals in all the major processes at the Blue Plains WWTP, Kim et al., (2002) identified the solids handling processes as the major on-site odor source.

Biosolids

Wastewater treatment processes produces two end-products, treated wastewater ready for discharge, and biosolids. The Blue Plains WWTP is producing biosolids of about 1,200-1,350 dry tons per day. Biosolids is mainly organic matter but contains some inorganics settled at the head of the plant and some metal-based inorganics coming

from the coagulants added during treatment processes, in the case of Blue Plains, ferric chloride.

Biosolid composition is highly dependent on types of water treated, i.e., either industrial or domestic, and the season of year. Biosolids are composed of about 30 % organic carbon, 2.5 % total nitrogen, 1.8 % total phosphorus, 1.1 % total sulfur, 3.8 % calcium, and less than 1 % of potassium, sodium, magnesium, iron, aluminum, copper, nickel, zinc, and others (VanLoon, 2000). In the past, biosolids have been disposed of by land filling, incineration, or ocean dumping, but because of growing concerns for the environment, and growing population and land demands, biosolids disposal has begun to lean towards its utilization as soil amendments in agricultural lands (Metcalf and Eddy, 2003). Biosolids build up the soil organic matter content in the same way as compost and manures do, thus improve soil structure and water retention capabilities and can provide significant amounts of soil nutrients (VanLoon, 2000). New requirements that have been implemented on biosolids land application practices is, however, limiting land application programs (Metcalf and Eddy, 2003). Biosolids quality therefore needs to be improved for land amendments, especially from the biosolid odor perspective. Biosolids at storage facilities are currently monitored by program managers at the plants in order to determine their destination, the least odorous batches are assigned to the most sensitive areas and the less odorous ones to more sensitive application sites (Rynk, 2003).

Currently used Odor Measurement Methods

Released odors are perceived as a nuisance and can lead to neighbors lodging complaints against the treatment plants. Accurately measuring odors and comparing them to human perception is extremely difficult, expensive, and a time-consuming

process. Odor measurements can be either sensory or analytical. The sensory measurements utilize human nose (i.e., olfactory sense) to assess odor quality. Analytical techniques quantify individual chemical compounds causing odor to the human nose. Unfortunately, both methods have their flaws; one cannot always be directly related to the other. Sensory measurements are very subjective and vary from person to person. Analytical measurements may not be directly related to human perception.

Odor Panel Evaluation

Forming a panel and questioning them about their perception of odors and the degree of annoyance is the most common odor assessment method (Francesco, 2001). These odor panels are still widely used for measuring odorants coming off not only wastewater biosolids but also compost (Canovai, 2004). Odor panel evaluations can be performed in three different ways; evaluating 1) odor concentration or odor strength by a dilution scale, 2) odor intensity using a relative intensity scale above threshold or a butanol scale, 3) hedonic tone using a pleasantness scale (Burlingame, 2004). For the results of the evaluation by an odor panel to be informative, each panel should be appropriately trained. Trained panels can make sensory judgments with ease as opposed to untrained people. An odor wheel can be used in wastewater applications as a basis for standardization, training, communication, and profiling of odor quality by panel sensory evaluations (Burlingame, 2004). Unfortunately, this method cannot differentiate between different individual odorants and mixtures and cannot give their exact concentrations since it depends on human olfactory sense. Difficulties in panel selection and prejudices spread among the residents also prevent this method from attaining the expected results (Francesco, 2001). Research has shown that different people perceive odors differently,

from offensiveness to odor thresholds. This is caused by a number of factors including age, familiarity to a particular odor, and whether or not a person smokes (Gostelow, 2001; Fenner, 1999; Stuetz, 2000). Nonetheless, since this method quantifies human response to odor sensation, it is still preferably utilized and significant efforts are being made to improve it especially in European countries (Gostelow, 2001).

The Electronic Nose

A lot of effort has been placed on research in an instrument that mimics human olfactometry for the last few years (Gostelow, 2001). The electronic nose system, consisting of an array of 5 to 20 sensors with overlapping sensitivities and a pattern recognition system (Francesco, 2001), has been used to quantify odors from water and wastewater (Francesco, 2001; Gostelow, 2001; Fenner, 1999; Stuetz, 2000). With an electronic nose equipped with a pattern recognition system, which requires extensive sensor calibration with human responses to odors, the presence of specific odorous compounds, odor concentration or odor characters can be evaluated (Francesco, 2001). However, since it uses real world data that are uncertain and vague, it can provide imprecise or incomplete measurements, background noise, or distorted information (Francesco, 2001).

Other methods for odor analysis involve a gas chromatograph (GC). Before the GC analysis, purge and trap methods are frequently applied to concentrate odorants within specific media. However, these purge and trap methods always surffer from problems associated with product yields due to the reactivity of the odorants (Shuler, 2002).

Odor Treatment

Odor has been treated in the off gasses by many different mechanisms but all involve the removal of the odorants from the gas phase followed by some sort of treatment. These treatments include but are not limited to scrubbers, adsorption, absorption, incineration, masking, and biotechnological methods. Scrubbers transfer the pollutant from the gas phase to the liquid phase by putting the odorous gas in contact with liquid absorbant. Selection of absorbent is dependant on the type of pollutants. It can be water (usually basic or alkaline) or solutions containing hypochlorite, chlorine dioxide, potassium permanganate, or ferric sulfate (Smet, 1998; Canovai, 2004). The odorants in the gas phase can be transferred to the bulk liquid by bubbling the gas through the liquid. The mass transfer efficiency is dependant on the surface area of the bubbles, the contact time, and the diffusion coefficient (Burgess, 2001).

Another technique is utilizing adsorption of odorants onto a solid medium. These media include silica gel, activated carbon, activated alumina, and synthetic resins among others (Shuler, 2002; Smet, 1998; Canovai, 2004). Activated carbon is widely used for wastewater treatment applications because it has large internal surface area per unit weight (Shuler, 2002).

Off gases from wastewater treatment processes can be incinerated, especially when odorant concentrations are very low. Although the incineration is a very efficient process, it is very costly (Smet, 1998).

Masking agents, for example terpenes, have been used to cover odors emitted from various sources, especially animal housing. If a masking agent is used in the open air or where aeration is provided, however, they can be diluted and lose their masking

ability. From this point of view, masking agents are not very effective for wastewater odor controls (Shuler, 2002; Smet, 1998).

Biotechnological methods for the removal of odorous pollutants from a gas stream can include bio-filters, bio-scrubbers, and bio-trickling filters (Metcalf and Eddy, 2003; Canovai, 2004). Biofilters are a packed bed of an organic carrier material (peat, compost, bark, or a mixture) on which biofilm is formed and through which the humidified gas flows. The biofilm then feeds on the odorants in the passing gas stream, breaking them down. Although it is efficient, it requires large reactor volumes and frequently has clogging problem (Smet, 1998; Metcalf, 2003; Burgess, 2001). Biofilter methods are often used in composting facilities which are small and can accommodate these types of treatment. A bio-scrubber is a tower where the pollutant contaminated gas stream is placed in contact with water that is fed to a bioreactor where the pollutant is biologically degraded (Smet, 1998). The last method is a bio-trickling filter which works just like a bio-filter except that the material used for the attachment of the biofilm is chemically inert (Smet, 1998; Burgess, 2001).

Oxidation-Reduction Potential

Oxidation-Reduction Potential (ORP) is one of the key parameters to the release of certain odorous compounds from wastewater and biosolids. An electron transfer from substrate to oxidant causes the oxidation-reduction reaction to occur and can be easily monitored using ORP probes (Chang, 2002). As was found by Paillard and Blondeau (1988), highly odorous volatile sulfur compounds are generated in WWTPs at redox potentials lower than -50 mV.

Odors can be reduced or eliminated in the liquid phase by adding chemicals for the purpose of chemical oxidation, chemical precipitation, and pH control. Among these, oxidation has attracted researchers' attention due to its effectiveness. The process utilized the nature of odorous chemicals; most odorous chemicals are formed under septic condition. Therefore, oxidation state of the system can be adjusted to minimize odor release. The chemicals commonly added in wastewater treatment processes include sodium hypochlorite, potassium permanganate, hydrogen peroxide, and ozone (Metcalf and Eddy, 2003). However because of the complex make-up of the biosolids, chemical addition varies greatly from plant to plant, depending on the origin of the sludge and the type of processes at the plant.

Oxidants

Biosolids should be stabilized before they can be hauled out and applied in the field. Through the stabilization, the metals can be immobilized, the microorganisms can be inactivated, and the release of odorous chemicals can be diminished. Many chemicals can be used for the purpose of stabilization but the most frequently used is lime. However, before the dewatering process, the production of reduced sulfur species can be lowered by adding an oxidant.

Reduced sulfurs are produced under anaerobic conditions which are indicated by a low or negative ORP value. Most sulfides are produced from the reduction of sulfate at ORPs of -250 to -300 mV while some are from the hydrolysis of proteins (Charpentier, 1998). Oxidizing the sludge not only reduces odor formation but also destroys organic matter (Jomaa, 2003). Zhang et al. (2005), found that by providing constant aeration they could reach removal efficiencies up to 95% for VFAs. Aerobic treatment improves the

oxygen supply to aerobic microorganisms that convert waste into stable end products thus preventing the activity of the anaerobic microorganisms that convert it into incompletely oxidized end products (Zhang, 2005).

The chemical oxidants chosen for this study are potassium ferrate (K_2FeO_4), sodium hypochlorite (NaOCl), calcium nitrate ($Ca(NO_3)_2$), and potassium permanganate (K_2MnO_4). All four have strong oxidizing power; 2.20 V for ferrate at acidic condition, 1.68 V for permanganate, 1.48 V for hypochrorite, and 0.88 V for calcium nitrate, and fast reaction rates (Jiang, 2002; LaGrega, 2001).

Potassium Ferrate

Potassium ferrate is a good oxidant for the purpose of wastewater because it is highly stable, and selective, and it forms a non-toxic Fe (III) byproduct unlike Cr(VI) and Mn(VII) (Sharma, 2002). It not only works well as an oxidant, but it can also be used for the purpose of coagulation and disinfection (Sharma, 2002; Jiang, 2003; De Luca, 1996). Fe(III), which is produced through ferrate oxidation, acts as a sink or coagulant for sulfides; it reacts with sulfides to form insoluble ferrous sulfide (Jiang, 2003; Picot, 2001). With its high oxidizing potential, ferrate (VI) can also be used as a disinfectant for wastewater (Jiang, 2003). Decomposition of ferrate in water happens usually in the form:

$$2FeO_4^{2-} + 3H_2O \rightarrow 2FeO(OH) + 1.5O_2 + 4OH^- \quad \text{Eq. 2.1}$$

Calcium Nitrate

Calcium nitrate works as an electron acceptor for denitrifiers, inhibiting the biological reaction of sulfate reducers that produce reduced sulfur compounds. In the

presence of nitrate, sulfate is not biologically converted to sulfide and the sulfide that is already present is slowly oxidized back into sulfates (Moody, 1999). When adding calcium nitrate to collection systems which are one of the major places of odor formation and release, the dissolved sulfide levels dropped to lower than 1 mg/L once they reached the conveyance systems (Moody, 1999). By adding calcium nitrate Leavey (2001) could reduce 91.5% hydrogen sulfide production. Calcium nitrate does not require constant mixing, since it is non-abrasive. It is easy to contain, apply, and transfer by pumps due to its low viscosity (Leavey, 2001; Moody, 1999). Calcium nitrate oxidation usually follows this pattern:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad \text{Eq. 2.2}$$

$$NO_2^- + 6H^+ + 6e^- \rightarrow N_2 + 4H_2O \qquad \text{Eq. 2.3}$$

Potassium Permanganate

Potassium permanganate contains manganese with a oxidation state of +VII. In general, as a result of oxidation, permanganate is reduced to insoluble manganese dioxide (Letterman, 1999). The insoluble manganese can act as an adsorbent for ferrous iron and several trace inorganic cationic species (Letterman, 1999). Since it is highly reactive, when used in oxidation processes, large quantities of potassium permanganate are required, resulting in higher operating costs. Oxidation by permanganate usually follows the form:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O \qquad \text{Eq. 2.4}$$

Sodium Hypochlorite

Sodium hypochlorite is commonly used as a scrubbing fluid. Sodium hypochlorite in scrubbers has chemical removal efficiencies all in the 90% range for hydrogen sulfide, ammonia, sulfur dioxide, and mercaptan gases (Metcalf & Eddy, 2003). Charron et al. (2004) found that when comparing sodium hypochlorite in scrubbing towers to hydrogen peroxide, it had a removal efficiency for methyl mercaptan of 97% versus 45%, because it leads to a mass transfer acceleration. Because of all these qualities sodium hypochlorite is a good choice for use in a wastewater setting. Disintegration of sodium hypochlorite in water first forms hypochlorous acid, which then oxidizes in this form:

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad \text{Eq. 2.5}$$

Sludge disposal is also a great concern for WWTPs, with disposal costs usually being anywhere from 30-60% of a plant's total operational cost (Horan, 1990). In the future, stricter regulations on sludge quality and disposal will cause an increase in the operational costs.

By maintaining ORP of activated sludge at a specific level (usually greater than -100 mV), Saby et al. (2003) could reduce the amount of excess sludge by up to 58% as compared to the conventional activated sludge process without an ORP control. One advantage of the oxidants chosen for this study was the ability to aid sludge dewatering. Unlike the other oxidants, ozone solubilizes or removes up to two thirds of organic matter in the sludge and enhances anaerobic digestion, but worsens dewaterability (Neyens, 2003). Other oxidants used in the past, were effective in solubilizing waste activated

sludge and increasing soluble chemical oxygen demand, and the sludge's biodegradability (Chang, 2002).

Sulfides, Amines, and Mercaptans

Nitrogen containing compounds, e.g., amines, indole and skatole are one of major odorants from WWTPs. These compounds are formed from urine, proteins, and amino acids. More specifically amines are naturally produced as metabolic products of microorganisms, plants and animals, via decarboxilation of amino acids and degradation of nitrogen containing compounds (Kataoka, 1996; Gostelow, 2001). Amines have an unpleasant odor and are hazardous to human health; they can irritate skin, eyes, mucous membranes and respiratory tracts (Gao, 1990). High levels of trimethylamine can be released if the biosolids pH is raised over its pKa (9.3).

The formation of methyl mercaptan and dimethyl sulfide in anaerobic environments can be derived from the microbial degradation of the sulfur-containing amino acids like S-methyl methionine, methionine, and S-methyl-cysteine, and from the methylation of sulfide (Kadota, 1972; Finster, 1990; Lomans, 2002; Smet, 1998). Reduction of dimethylsulfoxide and dimethyl disulfide under anaerobic conditions is another possible mechanism resulting in the formation of methyl mercaptan and dimethyl sulfide (Lomans, 2002). Lomans *et al* (2000) found that in sulfide-rich sediments, methyl mercaptan and dimethyl sulfide formation was greatly enhanced when methoxylated aromatic compounds like syringate and 3,4,5-trimethoxybenzoate were added. Mechanisms for production of the volatile organic sulfur compounds (VOSCs) are shown in Table 2.1.

Table 2.1: Microbial mechanism for VOSC degradation and production (Lomans, 2002).

Mechanism	Reaction
VOSC formation	
DMSP cleavage	DMSP → acrylate + DMS
MMPA demethiolation	MMPA → acrylate + MT
S-amino acid degradation	S-AA → HS^- / MT / DMS + AA
DMSO reduction	lactate (DMSO) → DMS + acetate
Sulfide methylation	
Detoxification	HS^- + R-CH_3 → R_a + MT
MA degradation	HS^- + R-CH_3 → R_b + MT
MT + R-CH_3 → R_b + DMS	
DMDS oxidation/reduction	DMDS ←→ 2 MT
VOSC degradation	
Oxidation	DMS / MT + O_2 → MT + CH_2O → CO_2 + SO_4^{2-}
DMS / MT + O_2 → MT + CH_2O → CO_2 + SO_4^{2-}	
Phototrophic oxidation	DMS / MT + H_2O → DMSO
Oxidation to DMSO	DMS + O_2 → DMSO
Denitrification	DMS / MT + NO_3^- → N_2 + CO_2 +SO_4^{2-}
Methanogenesis	DMS / MT → CH_4 + CO_2 + HS^-
Sulfate reduction	DMS / MT + SO_4^{2-} → CO_2 + HS^-

Note: MA, methoxylated aromatic compounds; DMSP, dimethylsulfoniopropionate; MMPA, methylmercapto-propionate; S-AA, sulfur-containing amino acids; AA, amino acids; MA, methoxylated aromatic compounds; DMSO, dimethylsulfoniopropionate; $R_{a,b}$, variable residue, group or compound; DMS, dimethyl sulfide;p MT, methionine.

Forms of Analysis (amines, sulfides)

Determination of amines in wastewater has generally been limited to three approaches: (1) directly analyzing aqueous sample by injection into a GC (2) concentration of the amines, separation, and detection, and (3) derivatization of the amines (Pan, 1997). Because of their high polarity, volatility, water solubility, and basic characters, free amines cannot be easily extracted or chromatographed (Abalos, 1999). Their high polarity even causes a peak tailing in the chromatograph on a non-polar column commonly used for volatile analysis. Amines also tend to be absorbed and decomposed on the column giving tailed elution peaks, resulting in ghosting phenomena and low responses from the instrument (Kataoka, 1996). Therefore, a proper column should be chosen to obtain enhanced GC responses.

Sulfur compounds, especially thiols containing a -SH group, are difficult to measure at low concentrations because of their reactivity; for example they adsorb well on the surface of glass and metal. So, direct injection of gas samples into a GC can lead

to low or no response (Tangerman, 1986). Past techniques involve a step to pre-concentrate odorant of interest. These techniques include solid absorption, liquid extractions, wet chemical or impregnated filtering techniques, chemisorption onto gold foil, trapping by chemical reactions with mercury salts and liquid argon, or cryogenically trapping the compounds (Tangerman, 1986; Smet, 1998; Gostelow, 2003).

Volatile Fatty Acids

Volatile Fatty Acids (VFAs) are also major odorants emitted at a WWTP. VFA's are low molecular-weight organic acids with a strong hydrophilic character (Narkis, 1978; Pan, 1995). VFA's are important metabolites or intermediates in biological processes and are widely dispersed in nature (Brill, 1991). They are formed through anaerobic-biological degradation of carbohydrates, proteins, and fats (Abalos, 2000; Gostelow, 2001). Sato et al (2001) found that about 90% of the odor-causing substances in human waste were fatty acids consisting of acetic, propionic, and butyric acid. Oxygen unavailability was found to be the main cause of VFA persistence in swine waste slurries; air can eliminate the VFA's and their precursors (Cooper, 1978).

Forms of Analysis (VFAs)

Traditional VFA analysis involves sample pretreatment such as liquid-liquid extraction, distillation, or purge and trap, before a gas sample is introduced into a GC for separation and quantification. These past methods have been found impractical for the measurement of VFA's because they are found at such low concentrations that they require long sampling times and many concentration steps (Spinhirne, 2003). Since these chemicals are highly polar, volatile, and less soluble in water, a derivatization is often

performed (Abalos, 2000). Because of all these setbacks and long sampling time of the traditional techniques, a new method needs to be developed.

Solid Phase Micro-Extraction (SPME)

Solid phase micro-extraction (SPME) has shown to be not only a method that is sensitive enough to detect odorants at low concentrations, but one that does not require the long sample preparation and steps that can cause errors and loss of analytes.

Headspace SPME is a solvent-free sample preparation technique in which a fused silica fiber coated with polymeric organic liquid is introduced into the headspace over the liquid matrix of a sample (Zhang, 1993). SPME has been successfully applied to the analysis of volatile compounds in various matrices. The extraction process is generally the step where most of the analyte loss and interference from the sample matrix occur (Zhang, 1993; Steffen, 1996). Using SPME sample extraction can be done on site. Since it extracts small amount of analyte, interference from sample matrix can be minimized.

Sampling with a SPME fiber can be performed under flow conditions, in which an inert gas or air is flushed, or under static conditions. If it is carried out under flow conditions, a number of equipment is required on site (Haberhauer-Troyer et al., 1999). SPME has been used in a number of applications; various fiber coatings have been applied to measure various analyte. There are several stationary phases available for the different types of compounds (Zeng, 2002**);** these which include carboxen-divinylbenzene, polydimethylsiloxane-divinilbenzene, carbowax-divinylbenzene, and others.

For the case of free volatile amines, Abalos et al. (1999) found that when comparing carboxen-PDMS fibers to PDMS fibers, the carboxen-PDMS fiber showed 4

to 10 times higher area counts. However, Kim et al. (2001) and Steffen et al. (1996) showed better results with the polyacrylate fiber coating for use on VFAs. Researches have shown that responses from a GC after SPME were linear over the odorant concentrations of two to three orders of magnitude and that method detection limits can fall down to the concentration comparable to human olfactory thresholds (Kim et al., 2002; Abalos et al., 1999, Pan et al., 1997). SPME coupled with derivatization leads to significant improvement in sensitivity for the determination of polar fatty acids (Pan, 1997). The use of SPME for VFAs was also demonstrated by Spinhirne et al. (2003), who used a DVB/Carboxen/PDMS fiber with an exposure time of one minute in a rumen fermentation system. The PDMS fiber coating is non-polar and has been known to work very effectively on a wide range of analytes, both polar and non-polar. Therefore, whenever SPME is applied to extract a chemical from a matrix, PDMS coated fibers are usually first tested, since this coating also shows a high affinity for polar compounds although it is apolar (Eisert, 1997).

The wide use of SPME for the analysis of volatile compounds proves that SPME is an improving and highly sought-after analytical method. It has been applied in the food industry for the analysis of odorants coming off wine, milk, and various juices, in the public health for the analysis of odorous compounds in human breath, and in the environmental science and engineering for the analysis of water samples from various sources (Pawliszyn, 1997).

Chapter 3: Analysis of Sulfides, Amines, Mercaptans, and Volatile Fatty Acids of Wastewater and Sludge Using Solid Phase Microextraction under Static Condition

Abstract

Odors are the biggest concerns and restraints in wastewater, composting, and animal waste management. Quantitative analysis is necessary in order to minimize the release of these odorous compounds and to keep complaints to a minimum. An analytical method using solid phase microextraction was developed to quantify several predetermined odorous gases. A static Teflon chamber with gas standards produced with certified permeation devices was used to expose the fibers to the odorous compounds. Two types of fibers were used; a fiber with a 75-µm carboxen-poly-dimethylsiloxane (Car-PDMS) coating for the analysis of trimethylamine, methyl mercaptan, carbon disulfide, ethyl mercaptan, dimethyl sulfide, propyl mercaptan , butyl mercaptan, and dimethyl disulfide, and the other fiber with an 85-µm polyacrylate coating for the analysis of acetic acid, propionic acid, butyric acid, iso-butyric acid, valeric acid, iso-valeric acid, and para-cresol. The method used a one hour exposure time with detection limits ranging from 0.0004 to 2.9943 ppmv for the Car-PDMS fiber and from 0.0228 to 2.3309 ppmv for the polyacrylate fiber. All standard curves showed R^2 greater than 0.99.

Introduction

Odor analysis and control is a major issue for wastewater, composting, and animal industries. Identification of the particular chemicals associated with emissions from different processes within a wastewater treatment plant (WWTP) along with analysis of detailed information on the plant operating conditions is required to accurately describe how those processes promote production of odorous gases.

Olfactometry and odor panels are frequently used to quantify or analyze odorants coming off not only wastewater biosolids but also compost (Canovai, 2004). A human's response to an odor is, however, highly subjective; different people find different odors offensive at different concentrations (Gostelow, 2001). Also, olfactometry does not allow for the differentiation and quantification of the individual odorants present in a gas sample.

Another method commonly applied for the analysis of odorous compounds is the electronic nose, however this technology is still developing. Using an array of chemical sensors developed to identify simple or complex gas mixtures, the electronic nose can detect odors coming off different types of samples (Hobbs, 1995; Di Francesco, 2001; Ziegler, 1998).

There are many different chemical odorants present in biosolids. Reduced sulfur compounds such as sulfide and mercaptans and volatile fatty acids (VFAs) are significant contributors to odors from wastewater processing (Hwang, 1995). Domestic wastewater typically contains 3-10 mg/L organic sulfur, derived mainly from proteinaceous material (e.g., sulfur containing amino acid) and sulfonates originated from household detergents

(Boon, 1995; Harkness, 1980). They can also be formed from reactions between H_2S and unsaturated ketones (Harkness, 1980).

Volatile fatty acids are the by-products of carbohydrate fermentation and are generally associated with anaerobic treatment, especially the anaerobic treatment of wastewater sludge (Bonnin, 1990; Abalos, 2000; Manni, 1995; Narkis, 1980;Jen, 1993; Lie, 1997). They are also formed from humic substances in water treatment processes, and because of the strong hydrophobicity of these compounds, especially the short chain ones (2C-5C), they do not remain within water and become difficult to analyze with high precision and efficiency (Pan, 1995; Brill, 1991).

Not much work has been done on the analysis of very reactive and odorous compounds of wastewater and biosolids using solid phase microextraction (SPME), although the method has been applied for quantification of organics in various matrices. Kim et al. (2002) developed a method to analyze volatile sulfur and fatty acid compounds by utilizing SPME for sample extraction and a gas chamber along with a permeation device to produce standards gas. Their method eliminated some of the problems encountered in the production of standards and in the collection and analysis of the samples. Past practices making gas standards include ones utilizing Teflon bags or stainless steel containers (Murray, 2001; Sato, 2001; Zhang, 1993), in which a known concentration of liquid chemical is spiked and then diluted to a known volume with an inert gas, usually high purity nitrogen or helium. These methods have proved to be tedious and can lose analytes, if stored for a period of time, because of adsorption on the surface of the containers. The chemical compounds can also react with the material in the bags or containers changing the final concentration (Murray, 2001; Sato, 2001;

Zhang, 1993). Some companies can make standards of several chemicals in a pressurized stainless-steel container, but these also can react over time with the material of the tank and end up producing significant errors in calibration (Haberhauer-Troyer, 1999; Zhang, 1993).

By introducing a systematic analytical procedure utilizing SPME fibers, Kim et al. (2002) made it easy to collect and concentrate analytes in gas phase and to quantify with gas chromatography (GC) with high reproducibility and precision. However, their method has some disadvantages. In their method, a SPME fiber is exposed to a gas sample flowing at a certain velocity (i.e., 72 mL/min). In fact, in the field, a constant flow of a gas is difficult to provide and the method would require the transport of a delicate pump. The method proposed by Kim et al. (2002) is more likely to measure an hourly average concentration of odorants in the air. Therefore, their method is limited in being applied in places where analysis is done on grab samples at a specific time.

In this paper, therefore, a new method to quantify specific odorants in gas samples at static condition using SPME coupled to two GCs in series (one with flame ionization detector (FID) and the other with mass spectrometer (MS)) is presented. A total of 15 predetermined compounds which have been reported as major odorants released from WWTPs were quantified; they include trimethylamine (TMA), carbon disulfide (CDS), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), methyl mercaptan (MM), ethyl mercaptan (EM), propyl mercaptan (PM), butyl mercaptan (BM), para-cresol (PC), acetic acid (AA), butyric acid (BA), propionic acid (PA), valeric acid (VA), iso-valeric acid (IVA), and iso-butyric acid (IBA). A procedure to collect/extract gas samples and to quantify the extracted odorants using the developed method is also presented.

Experimental methods

Calibration method for SPME

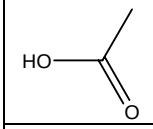
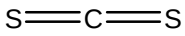
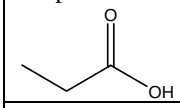
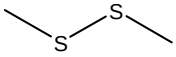
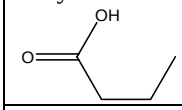
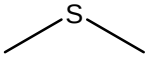
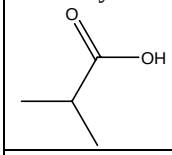
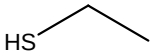
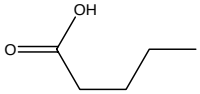
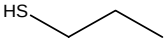
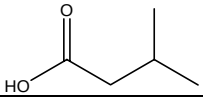
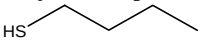
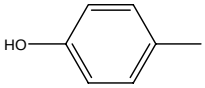
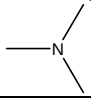
Standard gases for calibration of new method were produced using Teflon membrane-made permeation devices, in each of which is filled with a desired chemical in liquid or gas phase. These permeation devices release gaseous odorants through membrane at a constant rate. In this study, all the permeation devices were purchased from from VICI Metronics, Inc. (Santa Clara, California) except the methyl mercaptan device, which was purchased from Kin-Tek (La Marque, Texas). All the devices were NIST-certified traceable, and Teflon-made. The permeation devices were placed inside a temperature controlled gas permeation chamber within a Dynacalibrator, a gas generator (Model 320, VICI Metronics, Inc., Santa Clara, California), where high purity (99.99 %) nitrogen gas flowed at a base flow rate of 72 ml/min; for production of the methyl mercaptan standard gas, the permeation device was placed under high purity helium gas (99.99%). The maximum concentration of odorants was calculated based on the permeation rate of each device (Table 3.1) and the base flow (Eq. 3.1). Additional dilution gas was provided in order to make standard gas with lower concentrations.

$$Maximum\ Conc.\ of\ \ an\ Odorant = \frac{Mass\ Permeation\ Rate}{Base\ Flow\ Rate}\left[\frac{Mass/Time}{Flow\,Volume/Time}\right] \quad \text{Eq. 3.1}$$

Once permeation devices were placed inside the permeation chamber, they were allowed to equilibrate at its certified temperature (Table 3.1) for at least a day before a standard gas sample was taken. Whenever the dilution gas flow rate was changed to

produce a gas with a different concentration, at least three hours of equilibration time was allowed.

Table 3.1: Mass permeation rates and maximum concentration of different chemicals analyzed.

Compound	Perm. Rate, ng/min	Temp., °C[a]	Max. Conc., ppmv	Compound	Perm. Rate, ng/min	Temp., ° C[a]	Max. Conc., ppmv
Acetic Acid 	400	30	2.2628	Carbon Disulfide 	9	40	0.0402
Propionic Acid 	90	70	1.8665	Dimethyl Disulfide 	4.2	30	0.0172
Butyric Acid 	80	30	1.5222	Dimethyl Sulfide 	7.08	30	0.0387
Iso-Butyric Acid 	100	70	0.3856	Ethyl Mercaptan 	75	30	4.7571
Valeric Acid 	407	70	1.3538	Propyl mercaptan 	30	30	1.8513
Iso-Valeric Acid 	400	70	1.3305	Butyl Mercaptan 	30	30	1.7479
Para-Cresol 	665	100	2.0891	Trimethyl Amine 	75	30	0.4310

[a]Temperature at which each permeation device was certified.

The SPME fibers were exposed to the standard gas flowing though a Teflon-made cylindrical collection chamber (i.d. = 4.1 cm, Savillex Co., Minnetonka, Minnesota) placed at the outlet of the Dynacalibrator. The collection chamber contains two injection ports, sealed with a Teflon coated septa and an insertion hole for a temperature probe (Traceable –4085, Control Com., Houston Texas). Each end of the collection chamber was equipped with a valve to shut off the gas flow and leave the gas with a specific

concentration inside. Septa were only used once to avoid variation from potential leak through with each injection. The fibers were exposed at room temperature (20 +/- 2 ^{o}C) and an atmospheric pressure of 1 atm, which was assumed to remain constant.

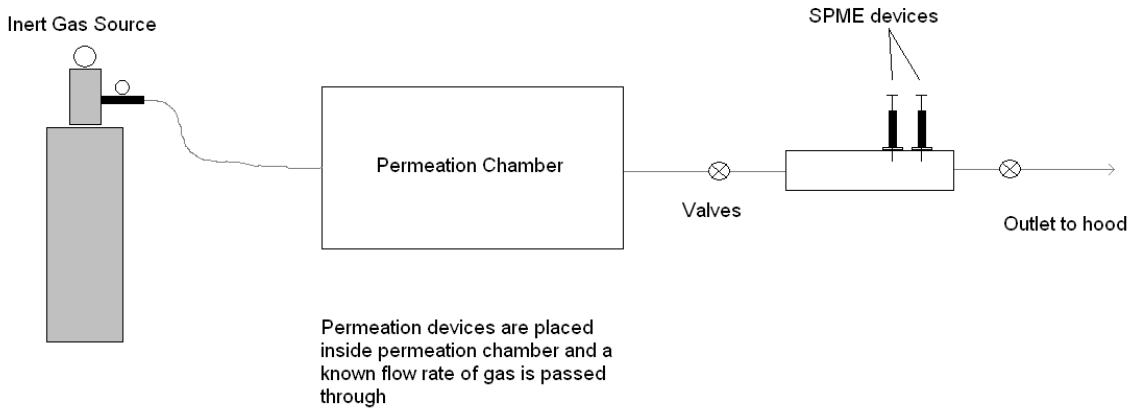


Figure 3.1:Experimental setup. Inert gas flowing into Dynacalibrator (permeation chamber), through Teflon sampling chamber and out to a fume hood.

GC System and Temperature Program

Analytes adsorbed on the SPME fibers were quantified using a gas chromatograph (GC) system, which is composed of two Agilent 6890N GCs in series (Fig. 3.2). The first GC (GC-1) contains an injection port equipped with a Merlin Microseal Septum (Supelco, Bellefonte, PA) designed for SPME fibers, a 0.75 mm injection port liner, and a FID. The second GC, (GC-2) is connected to an Agilent 5973 MSD, and a Gerstel Olfactory Detection Port (ODP). The MSD on GC-2 is set to Selected Ion Monitoring mode (SIM). The ions monitored for each analyte are provided in Table 3.2 along with their relative abundance.

Table 3.2: Scan mode times and Ions for the GC-MS

Compounds	**Ions (mass (dwell))**	**Compounds**	**Ions**
TMA and MM	45 (60%), 47 (100%), 48 (90%), 58 (100%), 59 (50%)	AA	43 (100%), 45 (60)
CS2, EM, and DMS	44 (50%), 46 (40%), 47 (60%), 62 (100%), 76 (100%)	PA and IBA	43 (60%), 45 (60%), 57 (30%), 73 (100%), 74 (100%)
PM	43 (60%), 76 (100%)	BA	60 (100%), 73 (50%)
BM	56 (100%), 90 (99%)	IVA	41 (50%), 60 (100%)
DMDS	45 (60%), 79 (60%), 94 (100%)	VA	60 (100%), 73 (60%)
		PC	77 (50%), 107 (100%), 108 (60%)

The two GCs are connected with a cryo trap system (Gerstel CTS1, Baltimore, MD) in which a 1 m long HP-5 column, 0.32 mm inner diameter, and a phase thickness of 0.25 µm is placed. The column installed on GC-1 is a 30 m HP-1, with an inner diameter of 0.32 mm and a phase thickness of 1 µm. A 30 m DB-Wax column with an inner diameter of 0.32 mm and a phase thickness of 0.5 µm was installed on GC-2.

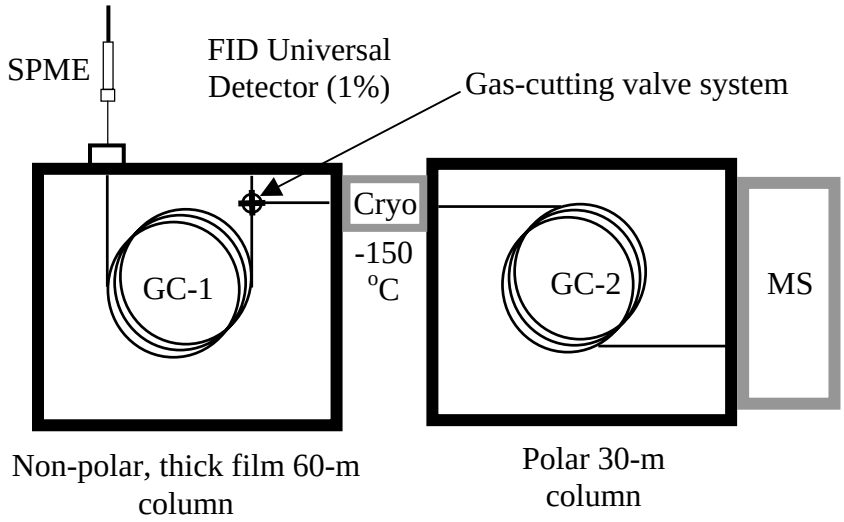


Figure 3.2: Schematic diagram of GC system used in current study.

When an injection is made, analytes are introduced into GC-1, where only analytes of interest can be chosen from chromatogram from the FID, and sent to the cryotrap set at -150 ºC by a so-called gas-cutting valve system (Gerstel, Baltimore, MD).

The analytes are frozen and re-concentrated in the cryotrap before they are heated and re-released into the GC-2. 93 % of analytes introduced into the GC-2 are split into the ODP and 7 % into the MS. Since only gases with chemicals of interest flowing through the column of GC-1 can be selected (cut) using the gas-cutting valve, it was possible to avoid introducing impurities into the MSD and to develop a clearer chromatogram. It also allows extending the lifetime of the MS filament. Table 3.3 shows times when cutting was done for sulfides, TMA, VAFs, and PC.

Table 3.3: Cuts selected for MS analysis.

Cuts	Sulfides and Amine			VFA's and p-Cresol		
	Start	End	Compound	Start	End	Compound
1	3.80	5.50	TMA, MM	3.80	4.60	AA
2	7.20	8.30	CDS, EM, DMS	4.85	5.50	PA, IBA
3	11.50	12.10	BM, PM	5.85	7.20	BA, IVA, VA
4	12.30	13.10	DMDS	9.50	10.14	PC

The signals obtained from the FID give a clear picture of the amount of chemical compounds that are found in the sludge. By first passing it through an FID, you can filter out the chemicals that you do not want to analyze for and can therefore get clearer MS chromatograms. The ODP-2 is a sniffing port that combines humidity with the specific compound that is picked up at that time by the MS. This sniffing port allows the operator to take a whiff of each chemical compound individually, allowing for comparisons to the overall smell of the sample. Unfortunately in our case, the concentrations that are picked up by the SPME fiber, are too low for the human nose to smell. A pre-concentration step would have to be included in order for this feature to have been useful. Because this feature also allows only for the analysis of about 7% of the gas, it decreases MS

sensitivity by a lot. Taking out this feature would require major instrument modifications and so was left on because MS detection limits were still reasonable.

Two different sets of temperature programs to analyze the chemicals adsorbed on Car-PDMS fibers and polyacrylate were made, respectively. GC-1's temperature program for the CAR-PDMS fiber starts at 32°C and holds for 3 minutes, then ramps at 3.5°C/min to 118°C, then at 50°C/min to 270°C. GC-2's temperature program for the CAR-PDMS fiber has an initial time of 13.5 min at a temperature of 32°C, ramps at 5°C/min to 45°C, holds for 2 minutes, then at 5°C/min to 90°C, then ramps again at 63°C/min to 250°C, and holds for one minute.

The temperature program for the polyacrylate fiber on GC-1 had an initial temperature of 110°C for 4 minutes, ramped at 9°C/min to 200°C, then 15°C/min to 270°C, hold for 2 min. The temperature program on the GC-2 for the polyacrylate fiber had a starting time of 13 min at 40°C, ramped at 8°C/min to 180°C, then at 50°C/min to 250°C.

The temperature program for the cryotrap system is set to start 10.50 minutes after an injection on GC-1 is made for Car-PDMS fibers for sulfide and TMA analysis. In the case of polyacrylate fiber, it is set to start 13.5 minutes after an injection. Once it begins, the temperature of the cryotrap system increases from -150 ^{o}C to 270 ^{o}C at a rate of 20 ^{o}C/min for both cases.

Figure 3.4 shows a chromatogram of sulfides and TMA from the proposed method using Car-PDMS fiber and one of VFAs and PC using the polyacrylate fiber. A good separation of peaks was found using this method, although the column was not intended for use with the VFAs and PC and so a definite tailing is evident after each

peak. This tailing can be improved if a column that is more selective for these highly polar compounds is selected. From these chromatograms it is evident that the column cutting system allows for the decrease of unwanted peaks and allows to easily identify and analyze the chromatogram.

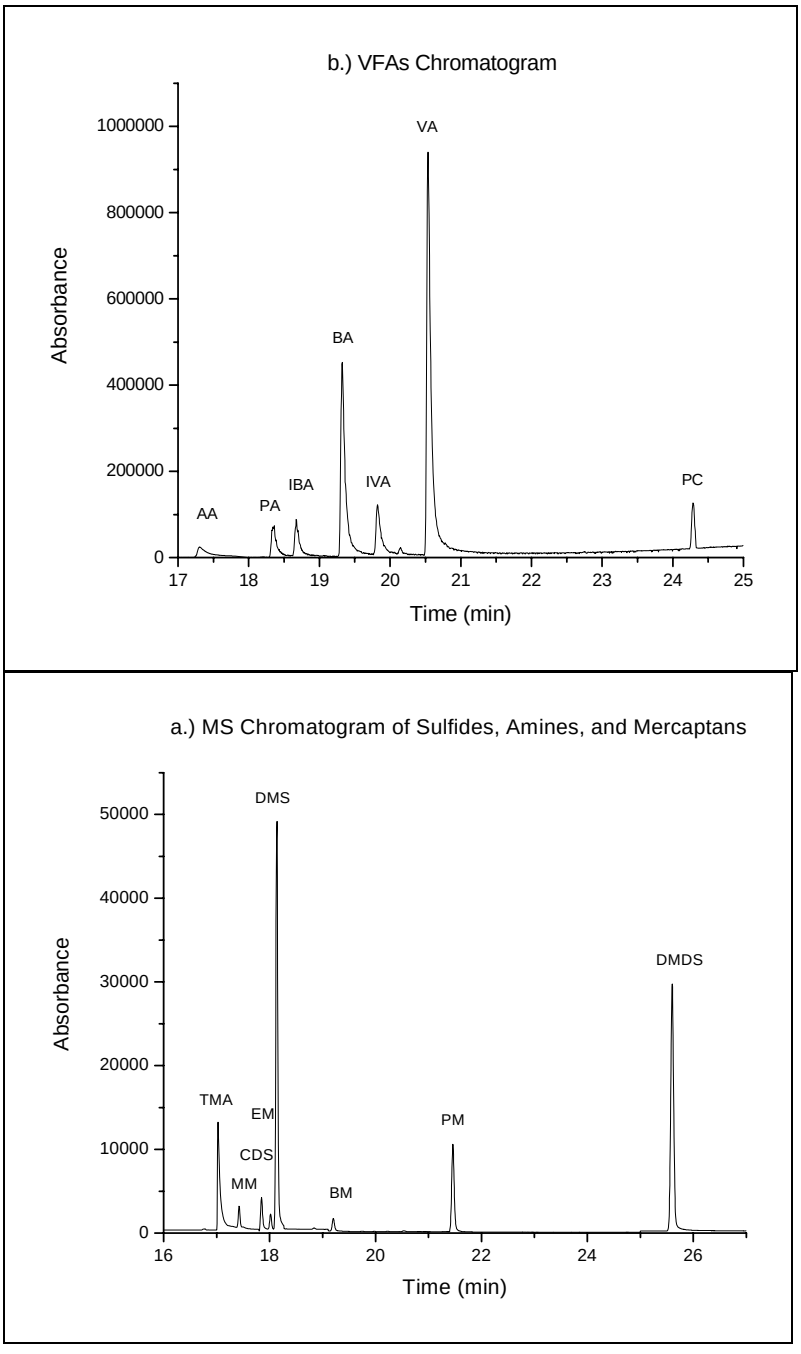


Figure 3.3: MS chromatograms for each of the 15 selected compounds (a.) sulfurs, b.) VFAs)

Results and Discussions

Equilibration time under static conditions

The mass of a compound absorbed by a SPME fiber is related to the concentration of the compound in the sample (Pawliszyn, 1997). The partition of the compound onto the SPME fiber (adsorption) initially takes place fast but slows down as it approaches equilibrium (Kim et al., 2002).

The partitioning time of the volatile compounds to reach equilibrium under static conditions have already been evaluated in past studies (Kim et al., 2002; Abalos et al., 2000; Bartelt, 1999; Pan et al., 1995). The equilibration time is not dependent on the concentration of a chemical but on the kind of fiber coating and on the nature of chemical compound itself (Pawliszyn, 1997). Although it is desirable to expose the fibers until equilibrium is reached, this can prove to be time consuming; about three hours of equilibration time was required for TMA, CDS, and DMS. Moreover, the partition of DMDS onto the fiber did not reach equilibrium even after 10 hours (Kim et al., 2002). Aromatic amines in the aqueous phase and sulfur compounds, such as MM and DMS, in the gas phase have been found to have equilibration times greater than 100 minutes (Haberhauer-Troyer et al., 1999; Muller et al., 1997). Therefore, a reasonable amount of time, one hour, is chosen to allow the fibers to absorb enough chemicals to be detected and is kept constant for all sampling.

Standard curves for sulfides, amines, and mercaptans

Using the proposed method, standard curves for sulfur compounds and TMA were developed and are presented in Fig. 3.4. All standard curves were made with at least five points and each point was repeated a minimum of five times; each point repeated with

different fibers. Correlation determinants (R^2) for the standard curves were all greater than 0.99 (Table 3.4). Errors associated with reproducibility range from 1 to 16 percent, the average error being 8 percent; errors were calculated by taking the standard deviation of the area readings for each concentration point and then diving by the average area value of all the readings at the same concentration. Butyl mercaptan showed the lowest R^2 value of 0.9907 while EM showed the highest R^2 value of 0.9997. The concentration range of sulfides and TMA for linear fit and the published odor threshold for each compound are also provided in Table 3.4. The lowest point for each compound is comparable with its odor threshold, although that for some compounds are rather higher than their odor threshold, for examples, EM and PM. However, considering errors associating with measuring their odor threshold, the concentration ranges for EM and PM can be regarded as comparable with the odor threshold. Unfortunately for the methyl mercaptan standard curve, a permeation device that was not contaminated with other compounds was never found. Data analysis and past research (Kim *et al.*, 2002), showed

Table 3.4: Linear fits summary and odor thresholds of analytes

Compound	Range (ppbv)	R^2	Odor threshold (ppbv)	Compound	Range (ppbv)	R^2	Odor threshold (ppbv)
MM	12.7-410	0.9997	1.1	AA	66-2330	0.9951	145
EM	12.7-410	0.9997	1.1	PA	32-1820	0.9905	33.5
PM	10.2-134	0.9957	1.3	BA	26-1180	0.9935	3.9
BM	4.1-109	0.9907	1.4	IBA	27-1500	0.9996	19.5
CDS	8-65	0.9917	95.5	VA	23-1320	0.9925	4.8
DMS	2.5-2990	0.9981	2.2	IVA	22.8-1300	0.9901	64
DMDS	0.4-585	0.9979	12.3	PC	26-2090	0.9995	1.9
TMA	7.5-110	0.9977	2.4				

that methyl mercaptan was able to be analyzed with SPME without the interference of other compounds, more specifically DMDS which was always present in the permeation device. In order to quantify methyl mercaptan, because of its similarities in chemical

structure and reactivity to ethyl mercaptan, the ethyl mercaptan standard curve was used when analyzing samples.

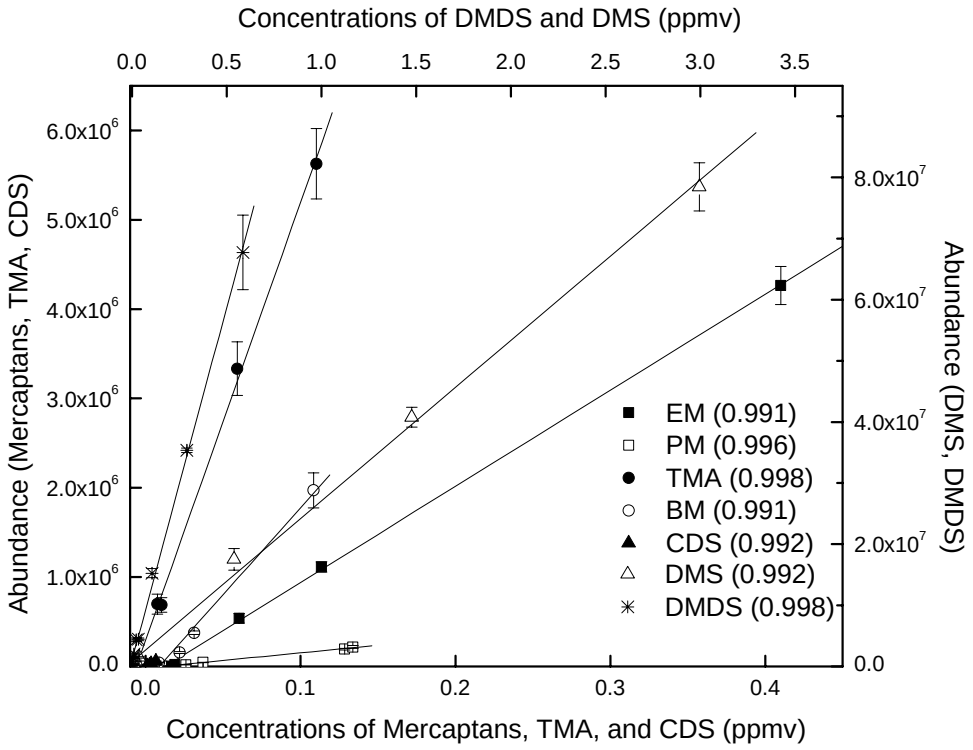


Figure 3.4: Standard curves for analytes of interest. R^2 provided in ( )

Standard curves for volatile fatty acids

Standard curves for VFAs and PC were also developed using the proposed method and provided in Fig. 3.5. Volatile fatty acids concentrations for linear fitting ranged from 0.0228 to 2.3309 ppmv. All standard curves had R^2 values greater than 0.99 ranging from 0.9903 for iso-valeric acid to 0.9995 for para-cresol. Errors per point range from 2 to 15 percent with the average error being at 6 percent for all the acids and PC. The fits for VFAs and PC are also summarized in Table 3.4. As in the case of sulfides, the lowest point for quantification for each compound is well comparable with human sensory odor threshold.

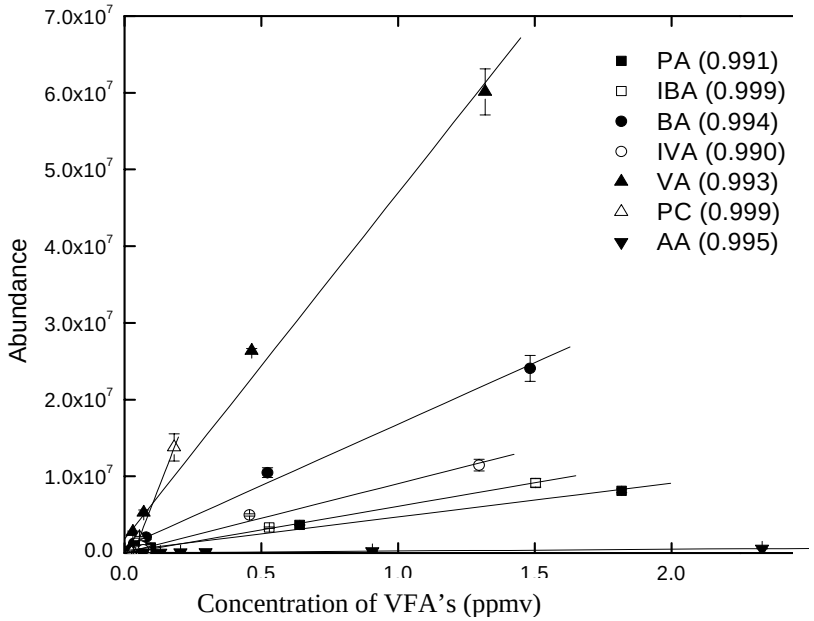


Figure 3.5: Standard curves for VFAs and PC. R^2 provided in ( ).

Suggestion of Procedure for Sample Analysis

In this section, a procedure to apply the method developed in this study is proposed (Fig. 3.6). Since the new method is based on static condition, sample analysis can be easily done. First, air sample is instantly collected using a Tedlar bag and a pump. Then a SPME fiber is inserted into the Tedlar bag and exposed for an hour on site. After a one-hour exposure, the SPME fiber is put in a cooler with dry ice and transported to a lab where GC analysis is performed. In this case, the Tedlar bag does not have to be big, since the extraction using a SPME fiber is not volume-dependent (Kim, 2002; Pawliszyn, 1997). Moreover, the gaseous compounds collected in Tedlar bags are extracted on site on to SPME fibers, the potential loss of compounds over storage time in the bags will be eliminated or minimized. Using the proposed analytical method and sampling procedure,

a grab-sample analysis, which is not possible with the method of Kim et al. (2002), can be implemented.

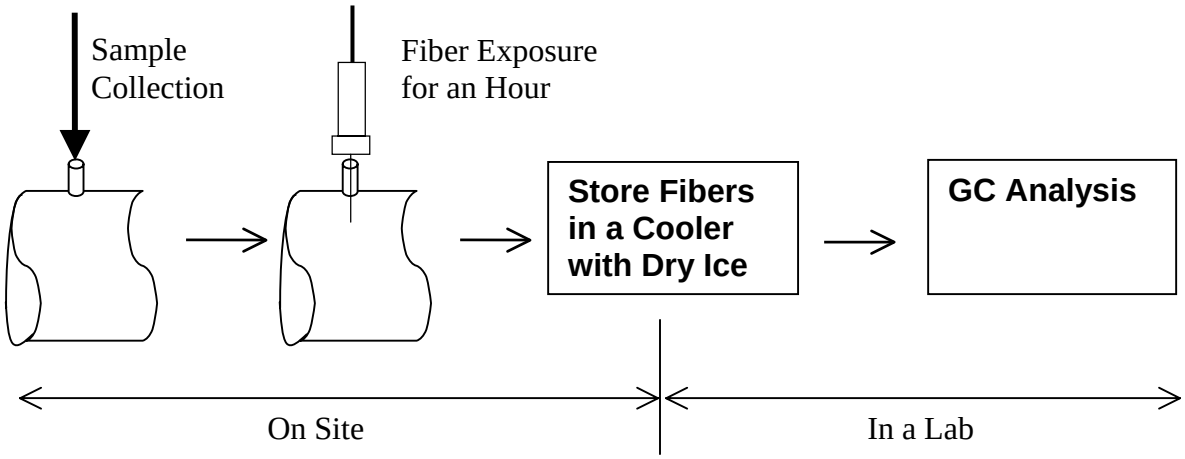


Figure 3.6: Proposed sampling procedure for utilizing developed method in this study

Conclusion

The current study has been performed as a sequel or improvement of the previous study performed by Kim et al (2002) on quantification of major odorants from wastewater or sludge. Comparing to the previous method, which utilizes increased adsorption capacity of SPME fibers to volatile compounds under flow conditions and requires a delicate pump to provide flow, the current method, which extract odorants under static condition with SPME fibers will be much easier to apply in the field for sample collection/extraction with minimum analyte loss. It was confirmed that even under the static condition, SPME fibers, if chosen appropriately, could extract volatile chemicals in the gas-phase enough to quantify levels comparable to human odor thresholds. As in the previous study, Car-PDMS fibers were found suitable for sulfides and TMA and

polyacrylate for VFAS and PC. Standard curves developed for each compounds under study showed linear with R^2 values always greater than 0.99 over a wide range of concentration.

We believe that the current method, if combined with the procedure suggested in this paper for field sample collection/extraction/analysis will allow research on odorants released from various wastes including wastewater and sludge to be performed much easier and inexpensively.

Chapter 4: Measuring Odorous Gases from Solids Processes of a Large Wastewater Treatment Plant

Abstract

Solids handling processes are important sources of odor in wastewater treatment plants (WWTPs). The odor quality of upstream solid handling processes will also control the character of the final biosolids product for land application. Odor-causing chemicals may be present in influent wastewater or they may be formed via degradation of organic matter during treatment processes. Key parameters such as pH, oxidation-reduction potential (ORP), metals concentration, polymer dosage and temperature can control production of such odorants as methyl mercaptan, dimethylsulfide, dimethyldisulfide, and p-cresol. A control scheme that requires feedback from within the WWTP system is needed to respond to conditions that enhance the production of odor-causing chemicals. However detailed simultaneous measurements of plant conditions and odorous chemical concentrations from different solids processes are required to design this control scheme to minimize the production of highly odorous biosolids. A large WWTP in Washington, DC was selected for this study. In the first stage, weekly grab samples have been collected from all major solids processes along with dewatered sludge for a year.

Along with numerous ancillary measurements to characterize the sludge, fifteen, key odorous gases were quantified in the headspace over sludge using solid phase microextraction (SPME) followed by analysis using gas chromatography-mass spectrometry. Target analytes included sulfide, mercaptan, amine, cresol, and volatile

fatty acid groups. Correlation between concentrations of odorous chemicals and sludge characteristics were made to determine operational and environmental factors controlling odor production. To assess contribution of each odorant to overall odor perceived by a human, odor index was evaluated. It was found that methyl mercaptan and dimethyl sulfide would have greatest impact on human perception of the odorants analyzed in this study. A correlation was found between ORP and the amount of sulfides released: the lower the ORP, the higher the odorants, specifically the reduced sulfurs released. The DAF thickened sludge and the blended sludge had the highest odorant concentrations and odor indexes, and were also the sludges with the lowest ORP measured. The dewatered limed cake was the only sludge in which TMA was always found because of the liming. The high TMA concentrations lead to a high odor index yielding high odor impact.

Introduction

Reduced sulfur compounds such as sulfide and mercaptans and volatile fatty acids (VFAs) are the significant contributors to odors from wastewater processing (Hwang et al., 1995). Domestic wastewater typically contains 3-6 mg/L organic sulfur, derived mainly from proteinaceous material and can contain further organic sulfur (about 4 mg/L) resulting from sulfonates in household detergents (Boon, 1995). The sulfur compounds can be derived from sulfur-containing amino acids, and they can also be formed from reactions between hydrogen sulfide and unsaturated ketones (Harkness, 1980). Volatile fatty acids are the by-products of carbohydrate fermentation and are generally associated with an anaerobic treatment, and in particular with the anaerobic treatment of wastewater sludge (Bonnin et al., 1990). Sato et al. (2001) found that about 90% of the malodor-causing substances in human waste were fatty acids consisting of acetic acid, propionic

acid, and butyric acid. Oxygen unavailability was found to be the main cause of VFA persistence in swine waste slurries. In the presence of air, as it is passed though the slurries, it not only eliminates the VFA's, but also their precursors, inhibiting formation after anaerobic conditions were reestablished (Cooper, 1978).

Complaints from the public due to nuisance odor have been one of the major concerns in the operation of many WWTPs, especially those in densely populated areas (Frechen, 1988, Wilson et al., 1980). Although all of the processes in WWTPs are a potential source of odor, those associated with the thickening/dewatering of the sludge, which concentrate proteins and other odor-causing organic chemicals, are generally the most significant. Especially under anaerobic conditions, the materials in solids handling processes decomposed to release odor causing compounds such as reduced sulfurs and amines.

Olfactometry and odor panels are frequently used to quantify or analyze odors. A human's response to an odor is, however, highly subjective; different people find different odors offensive at different concentrations (Gostelow, 2001). This is due to many different factors including age, familiarity to the particular odor or adaptation, and whether or not a person smokes (Gostelow, 2001; Fenner, 1999; Stuetz, 2000). Also, olfactometry does not allow one to differentiate and quantify the chemicals present in a gas phase. Identification of the particular chemicals associated with odor emissions from different processes within the plant along with analysis of detailed information on the plant conditions is required to accurately describe those processes that promote production of the most odorous gases.

In this project, the sludge characteristics and concentration of odors from solid handling processes under various operating conditions at The Blue Plains WWTP in Washington DC have been monitored over 12 months. The plant treats an average flow of 370 MGD of wastewater coming from the District of Columbia, Montgomery and Prince George's counties in Maryland, and Fairfax and Loudon counties in Virginia. The plant is in very close proximity to residential housing for the Naval Research Laboratory, a major interstate highway, Historic Alexandria, VA, and Reagan National Airport. This plant also has an extensive network of agricultural sites for land application of their biosolids. Public complaints due to on-site odor emissions and from neighbors living downwind from land application sites have led to increased regulatory action, fees, and transportation costs associated with disposal of the 1200-1350 dry tons of biosolids produced each day.

In the Blue Plains WWTP, sludges from primary and secondary sedimentation tanks are fed into gravity thickeners (GT) and dissolved air flotation (DAF) thickeners, respectively. DAF thickened sludge and GT thickened sludge are then combined in a blend tank from where they are withdrawn, mixed with polymer, and pumped into solid bowl decanter type centrifuges for dewatering. After centrifugation, the dewatered cake is conveyed for liming and then loaded on to trucks to be hauled for land application.

In the previous study on odor-causing chemicals in all the major unit processes at the Blue Plains, Kim et al. (2002) and Rynk et al. (2003) identified the solids handling processes as major on-site odor sources and suggested the investigation of system operating conditions to determine those factors that are critical in the generation of the most odorous chemicals. Rynk et al. (2003) explain that this high odor is bound in the

protein and their production is influenced by the following factors: a) the higher the concentration of iron and/or aluminum cations in the sludge appear to lower the odors coming off the dewatered cake, b) either mixing or storing the primary and waste activated sludge result in higher odors in the dewatered cake, c) and finally the higher the volatile sulfur compounds (VSCs) before digestion, the higher the odors in the cake.

This project, as a continuation of previous work, is designed to establish temporal trends in odor-causing chemicals generated from each unit process along with the sludge characteristics according to process conditions. The goal is to discover those critical parameters that cause the worst odor conditions and to ultimately develop control strategies for use in the plant to minimize odors within the plant and in the final biosolids.

Sample analysis is done via solid-phase microextraction (SPME) using a polyacrylate fiber for the volatile fatty acids (VFAs) and a carboxen-poly-dimethyl siloxane (Car-PDMS) fiber for the mercaptans, amines, and sulfurs.

Experimental Approach

Sample Collection

Sludge samples have been collected weekly from May 14, 2003 through May 5, 2004. Samples were obtained from several different locations within the plant's solids-handling system. Treatment processes, sampling location are summarized in Table 4.1:

Table 4.1: Sampling locations

Abbreviation	**Sludge**	**Sampling Location**
GR	Outflow from gravity thickener	Sample sink
DAF	Outflow from dissolved air flotation system	Sample sink
BS	Recycling line from Blending tank.	Sample sink
BSP	Blended gravity and DAF sludge from blending tank with polymer added.	Collection port just before centrifuge
DW	Dewatered sludge	Just after centrifuge, before conveyance
DWL	Dewatered sludge that has been limed in the laboratory	Just after centrifuge, before conveyance

The collected samples were divided into two sets; one for headspace chemical analysis and the other for ancillary characterizations for pH, ORP, total iron, calcium, and calcium carbonate concentrations, heterotrophic plate count, percent total solids, and total volatile solids. Lime was added to a sub-sample of dewatered sludge in the laboratory on-site. Analysis of percent solids was performed in the laboratory immediately after collection. Based on the solid content determined, the lime dose was adjusted to 20% by mass.

Extraction and Analysis of Odor Chemicals

For analysis of odorous chemicals, 5 mg of dewatered sludge or 10 ml of liquid sludge were placed in 20 ml vials, and sealed with an aluminum crimp top cap containing Teflon-coated silicone septum. The target analytes were pre-concentrated from the headspace over the sample using SPME. In SPME, a thin, coated fiber absorbs the organic chemicals from the headspace in proportion to their concentration. The fibers were exposed within the headspace for one hour. A 85 µm polyacrylate coating was used for VFAs, and a 75 µm Car-PDMS coating was used for the sulfur and trimethylamine chemicals. After exposure, fibers were transported (25 min) on dry ice to the USDA laboratory, where they were analyzed with a GC-MS system.

Table 4.2: Odorous compounds analyzed in this study.

Abbreviation	Chemical Name	CAS Number	Formula	Odor Threshold (ppb)	Detection Limits (ppb)
EM	Ethyl mercaptan	75-08-1	C2H6S	1.10	15.4
PM	Propyl mercaptan	107-03-9	C3H8S	1.30	10.4
BM	Butyl mercaptan	109-79-5	C4H10S	1.40	12.0
CDS	Carbon Disulfide	75-15-0	CS2	95.5	0.80
DMS	Dimethyl sulfide	75-18-3	C2H6S	2.24	4.60
DMDS	Dimethyl disulfide	624-92-0	C2H6S2	12.3	813
TMA	Trimethyl amine	121-44-8	C3HN	2.40	5.30
PA	Propionic acid	79-09-04	C3H6O2	35.5	20.1
BA	Butyric acid	107-92-6	C4H8O2	3.89	16.0
IBA	Iso-butyric acid	79-31-2	C4H8O2	19.5	17.6
VA	Valeric acid	109-52-4	C5H10O2	4.79	1.60
IVA	Isovaleric acid	503-74-2	C5H10O2	64.0	35.7

SPME fibers, which were not analyzed immediately, were preserved in a -40ºC freezer. None of the fibers were kept for more than 10 hours prior to analysis. The compounds shown in table 4.2 were extracted through SPME and analyzed by a multi-dimensional GC-MS system. After exposure, the fibers were desorbed in the injection port of the GC. The multi-dimensional GC-MS system consists of two, Agilent 6890N GC. The first GC (GC-1) is equipped with a flame ionization detector (FID) at a temperature of 250°C. The column for GC-1 is a 30 m HP-1, with an inner diameter of 0.32 mm and a phase thickness of 1 μm. The second GC (GC-2) installed with a 30 m DB-Wax column with an inner diameter of 0.32 mm and a phase thickness of 0.5 μm, is connected to an Agilent 5973 MSD at a temperature of 300°C. GC-1 and GC-2 were connected through a Gerstel CTS1 Cryotrap System, with a 1 m long HP-5 column (0.32 mm inner diameter, and a phase thickness of 0.25 μm). The injection port of the GC system was equipped with a 0.75 mm injection port liner and a Merlin microseal septum (Supelco, Bellefonte, PA) specially designed for SPME.

The temperature program on each GC for the analysis of sulfur compounds and TMA is as follows: initially, GC-1 holds at 32°C for 3 minutes, and ramps at 3.5°C/min to 118°C, then at 50°C/min to 270°C. GC-2 initially holds for 13.5 min at a temperature of 32°C, ramps at 5°C/min to 45°C, holds for 2 minutes, ramps at 5°C/min to 90°C, and then at 63°C/min to 250°C, and finally holds for one minute.

The temperature program for the analysis of volatile fatty acids is: the temperature of the GC-1 is initially set at 110°C for 4 minutes, ramped at 9°C/min to 200°C, then 15°C/min to 270°C, at which it is held for 2 min; the temperature of GC-2 initially holds for 13 mins at 40°C, ramps at 8°C/min to 180°C, and then at 50°C/min to 250°C.

Calibration Procedures

Preparation of the standard gases of each compound used in SPME calibration was done using certified Teflon membrane permeation devices (NIST traceable, VICI Metronics, Inc., Santa Clara, California, USA). The permeation devices were placed together in a thermostated glass chamber, where high purity nitrogen gas flows at 72 mL/min inside a gas generating device, Model 320 Dynacalibrator (VICI Metronics, Inc., Santa Clara, California, USA). The gas from the glass chamber is diluted with nitrogen gas at different flow rates to produce standard gases of desired concentration. Then the standard gas flowed through a Teflon cylindrical collection chamber (i.d.= 4.1 cm, Savillex, Co., Mennetonka, Minnesota) with two injection ports for SPME fiber exposure and a temperature probe (Traceable –4085, Control Com., Houston Texas). On both ends of the Teflon chamber a valve was equipped to shut off the gas flow. Both valves were shut at the same time and septa were replaced after each injection to avoid any leak of standard gas.

Before sampling, the middle point on the standard curve was checked in order to verify reproducibility and validity of the standard curve. Distilled water blank sample in an identical headspace vial was analyzed with each set of samples.

Results

Seasonal Concentration Variation of Each Odorants

Initial results indicate that overall concentrations were highest for the reduced sulfur chemicals and these were noticeably greater in the summer. Mean concentrations for each chemical measured in the study for summer (May – Aug), fall (Sept – Dec), winter (Dec-Mar), and spring (Mar-May) are provided in Table 4.3. Higher ambient

temperatures in the summer may have caused conditions in sewer lines entering the plant to become more septic thereby increasing the overall amount of reduced sulfur in the wastewater and sludge. Higher temperatures in the plant may also create more anaerobic conditions, thereby enhancing the production of reduced sulfur compounds. Butyric acid and carbon disulfide were found in higher concentrations in some processes only during the fall months.

All sulfurs and mercaptans were always found in every sample for all processes except for butyl mercaptan which was almost never found and propyl and ethyl mercaptan which were hardly found in the dewatered limed cake. Blended sludge and DAF thickened sludge released substantially higher concentration of DMS and DMDS than other processes, which is reasonable because the DAF sludge mainly consists of proteins, the source of sulfur compounds, originating from microbial cell decay and the blended sludge is a mixture of DAF and gravity. As observed in the previous studies (Kim et al., 2002), TMA was always released at high concentrations in the dewatered sludge after lime was added. It was also found from the blended sludge in the summer. All other sulfur compounds except DMS and DMDS were released at lower levels in sludge from every process. Methyl mercaptan was always present in every season and every process, however the highest concentrations were frequently found in the blended sludge with polymer. Acetic acid was found constantly and at the highest concentration for all the VFAs which were analyzed. Considering the human odor threshold for each VFA compound, these compounds may not contribute significantly to the odor character of the sludge which can be seen in odor index provided in Figure 4.2.

Table 4.3: Seasonal averages of pH, ORP and odorant concentrations for each process.

PROCESS		BS, ppbv	DAF, ppbv	GR, ppbv	BSP, ppbv	DW, ppbv	DWL, ppbv
pH*	Summer	6.41-7.76	6.88-7.82	5.69-7.10	6.47-7.02	---	---
	Fall	6.52-7.08	7.03-7.55	5.88-6.40	6.62-7.08	---	---
	Winter	6.66-6.83	7.03-7.33	6.05-6.47	6.73-6.92	---	---
	Spring	6.47-7.00	6.83-7.34	6.05-6.33	6.67-7.01	---	---
ORP*	Summer	-304 to -125	-358 to -247	-273 to -84	-284 to -205	---	---
	Fall	-296 to -171	-319 to -214	-189 to -108	-253 to -210	---	---
	Winter	-242 to -105	-266 to -229	-205 to -164	-230 to -190	---	---
	Spring	-222 to -180	-264 to -205	-158 to -194	-234 to -181	---	---
TMA	Summer	8.7(32.6)	ND	ND	ND	ND	123.9 (112.1)
	Fall	ND	ND	ND	ND	ND	52.2 (33.6)
	Winter	ND	ND	ND	ND	ND	43.3 (37.0)
	Spring	ND	ND	ND	ND	ND	50.2 (21.9)
MM	Summer	69.8 (57.2)	46.2 (30.4)	66.0 (52.9)	78.1 (56.0)	53.7 (22.4)	54.0 (34.6)
	Fall	18.9 (13.0)	19.7 (13.4)	29.0 (11.8)	46.7 (36.9)	52.3 (22.8)	13.8 (7.0)
	Winter	51.0 (28.5)	34.5 (14.7)	53.1 (32.4)	100.2 (71.7)	64.3 (22.5)	20.6 (7.8)
	Spring	24.3 (12.1)	22.4 (9.3)	30.4 (15.3)	48.4 (33.6)	34.6 (18.6)	14.2 (7.5)
CDS	Summer	1.9 (3.8)	0.6 (1.1)	1.4 (0.8)	0.7 (0.7)	3.1 (6.4)	2.0 (2.0)
	Fall	5.9 (14.8)	1.2 (0.4)	2.2 (2.2)	1.0 (0.4)	2.1 (0.8)	5.4 (1.7)
	Winter	1.5 (0.4)	1.0 (0.5)	1.6 (0.9)	1.3 (0.4)	3.5 (3.5)	17.3 (27.4)
	Spring	1.4 (0.2)	0.5 (0.6)	1.3 (0.2)	0.9 (0.6)	2.5 (0.8)	5.7 (2.1)
EM	Summer	9.4 (8.1)	7.1 (17.2)	11.3 (5.9)	2.9 (6.6)	6.7 (8.0)	ND
	Fall	3.4 (6.7)	0.7 (1.2)	3.4 (6.2)	8.8 (7.6)	1.6 (4.9)	12.0 (39.9)
	Winter	9.9 (7.7)	2.8 (1.6)	12.4 (5.5)	14.9 (0.0)	14.8 (0.4)	ND
	Spring	8.6 (8.0)	3.3 (2.5)	8.6 (7.1)	15.1 (0.3)	5.0 (8.6)	51.6 (136.5)
DMS	Summer	537.6 (461.0)	580.7 (646.8)	106.7 (67.2)	397.8 (434.4)	350.1 (250.3)	209.1 (170.9)
	Fall	77.8 (76.6)	61.6 (37.6)	37.3 (50.5)	147.4 (81.8)	214.2 (100.9)	100.6 (50.9)
	Winter	178.3 (111.9)	152.4 (187.2)	10.4 (7.0)	103.9 (98.6)	86.9 (53.5)	33.0 (17.0)
	Spring	249.5 (300.3)	175.9 (213.9)	18.9 (11.3)	93.2 (78.2)	162.4 (99.6)	79.9 (47.7)
PM	Summer	8.3 (6.9)	5.1 (7.3)	6.7 (7.6)	0.9 (1.0)	1.6 (5.5)	ND
	Fall	4.8 (6.7)	4.6 (6.4)	3.1 (5.7)	0.4 (0.7)	ND	ND
	Winter	9.3 (11.7)	6.3 (10.1)	4.9 (6.2)	0.4 (1.0)	3.2 (7.2)	ND
	Spring	2.8 (6.2)	1.9 (4.7)	4.7 (6.4)	0.7 (1.0)	3.3 (7.5)	ND
BM	Summer	ND	ND	ND	ND	ND	0.9 (3.3)
	Fall	ND	ND	ND	ND	ND	ND
	Winter	ND	ND	ND	ND	ND	ND
	Spring	ND	ND	ND	ND	ND	ND
DMDS	Summer	305.8 (294.3)	264.7 (297.3)	71.3 (49.5)	316.6 (240.5)	244.9 (127.2)	242.6 (142.7)
	Fall	19.8 (21.9)	20.4 (24.2)	26.7 (25.6)	103.0 (71.2)	271.3 (148.4)	54.4 (26.2)
	Winter	73.0 (73.3)	33.9 (35.1)	54.6 (100.6)	111.4 (60.5)	105.8 (61.7)	44.9 (51.9)
	Spring	33.0 (37.1)	25.1 (28.6)	18.2 (19.1)	71.6 (43.1)	198.2 (83.4)	79.8 (24.1)
PA	Summer	1.2 (4.3)	2.6 (9.9)	11.5 (27.5)	4.2 (11.9)	7.6 (14.7)	ND
	Fall	ND	ND	1.0 (2.4)	ND	ND	ND
	Winter	ND	ND	0.7 (1.7)	ND	1.3 (3.2)	ND
	Spring	ND	ND	ND	ND	ND	ND
IBA	Summer	ND	1.0 (3.8)	0.9 (3.4)	ND	ND	ND
	Fall	8.9 (13.6)	6.8 (8.7)	8.1 (10.1)	6.4 (10.6)	6.3 (8.4)	ND
	Winter	5.8 (10.1)	3.2 (7.9)	3.4 (8.9)	ND	5.3 (8.3)	ND
	Spring	11.2 (17.8)	11.2 (10.7)	2.6 (7.3)	12.0 (11.6)	10.0 (12.5)	12.1 (11.6)
BA	Summer	ND	10.1 (17.9)	3.4 (7.0)	6.9 (13.8)	30.3 (60.7)	8.2 (20.0)
	Fall	25.6 (72.5)	6.7 (16.7)	15.8 (35.6)	ND	ND	37.6 (71.1)
	Winter	ND	2.1 (5.4)	0.2 (0.4)	ND	ND	ND
	Spring	ND	0.4 (0.9)	ND	ND	ND	ND
IVA	Summer	ND	2.0 (3.5)	ND	ND	1.7 (1.7)	7.1 (12.2)
	Fall	ND	0.4 (1.2)	ND	ND	ND	ND
	Winter	ND	0.6 (1.7)	ND	ND	ND	ND
	Spring	ND	ND	ND	ND	ND	ND
VA	Summer	ND	3.4 (13.3)	ND	ND	ND	ND
	Fall	ND	ND	ND	ND	ND	ND
	Winter	ND	ND	ND	ND	ND	ND
	Spring	ND	ND	ND	ND	ND	ND
AA	Summer	382.9 (191.9)	227.1 (185.9)	2013.9 (6326.1)	391.4 (338.6)	203.4 (170.7)	260.7 (242.9)
	Fall	278.3 (412.0)	115.6 (122.1)	119.5 (223.9)	123.4 (223.3)	223.5 (251.5)	110.7 (136.1)
	Winter	236.1 (421.1)	156.9 (383.4)	228.9 (414.3)	44.4 (77.9)	202.0 (301.7)	14.3 (31.9)
	Spring	192.1 (133.1)	183.6 (157.3)	81.1 (113.1)	193.8 (168.2)	248.6 (248.1)	72.0 (91.1)
PC	Summer	56.1 (28.5)	49.0 (72.2)	62.3 (2.8)	54.6 (36.1)	63.1 (63.4)	30.7 (32.4)
	Fall	11.1 (24.7)	ND	20.6 (30.4)	6.0 (19.1)	10.1 (24.7)	ND
	Winter	20.1 (31.1)	17.3 (29.5)	ND	10.0 (24.6)	15.3 (30.5)	ND
	Spring	31.4 (33.7)	ND	8.6 (22.8)	ND	ND	ND

* pH and ORP: Ranges Provided.

Operation Parameters during the Study

Oxidation-reduction potential measurement provides an indication of the anaerobic nature of the material. The more negative the value, the more reducing the conditions in the system, increasing the production of reduced sulfur compounds. Each process showed different pH and ORP values for each season (Table 4.3). Gravity thickened sludge was found to have the lowest pH and the highest ORP values with ranges from 5.67 to 7.1 for pH and from -273 to -84 mV for ORP. Blended sludges with and without polymer were usually around the same readings although the polymer addition seemed to lower the pH and increase the ORP in most cases. The pH range for blended sludge without polymer was 6.41 to 7.76 and ORP from –304 to -105 mV. The pH and ORP ranges of blended sludge with polymer were 6.47 to 7.08, and –284 to –181 mV, respectively. Compared to other sludges, the one from the DAF process showed relatively high pH and the lowest ORP values; 6.83 to 7.82 for pH and –359 to –205 mV for ORP. Kim et al. (2002) attributed the lower ORP values of DAF thickened waste sludge to the activity of the thickened microorganisms driving the conditions to anaerobic. As was found by Paillard and Blondeau (1988), highly odorous volatile sulfur compound emissions are generated in WWTPs at redox potentials lower than -50 mV. The results show that although the blended sludge and gravity thickened sludge ORP is sometimes higher than that of the DAF, the sulfurs found there are also higher than the numbers found in the DAF. This can be attributed to the blend ratio, because the more organic matter is found in the gravity thickened sludge, blend ratio also seems to have an impact on odorant results. On the days where more GR was added to the DAF, the BS had higher odorant concentrations (data not shown).

Odor Index

Since all chemicals have different human detection thresholds, concentration values must be normalized to provide some insights into how different chemicals may contribute to the overall odor of the material. Odor index cannot be used alone as a means for determining impact of an odorant on overall odor sensation to human noses because little is known about the relationships created by odorants together, but it still provides a way to see the relative contribution of each compound. Odor index values were calculated by dividing the average concentration of each compound by its odor threshold in a simplified approach similar to that of Brinton (1998). A comparison of average seasonal results from GT, DAF, BS, and DWL revealed that DMS and MM were the strongest odorants among the investigated compounds and that TMA's contribution was the highest the dewatered limed sludge (Figure 4.1). It also suggests that DAF has the highest odor indexes of all the processes included in this study followed by the blended sludge. These results may correlate with the sludge ORP values, since the DAF thickened sludge was the one that had the lowest ORP values. Blended sludge followed DAF with the lowest ORP values and also showed the second highest odor index. Of course there were other chemicals present in the headspace that were not measured in this study due to time constraints that need to be included in future work, i.e., hydrogen sulfide, ammonia. Additional work should be carried out to identify other unknown odorants maybe present in the headspace. The highest odorant concentrations were found in the summer and can be seen lowering for the winter and then rising again during the spring. Of the factors measured for characterizing the sludge samples such as ORP, pH, Fe content, Ca content, % solids, and VSS (Table 4.3, 4.4), only ORP exhibited a

statistically meaningful relationship with the release of odorous chemicals, especially sulfur compounds. Both DMS and DMDS were negatively correlated with the ORP

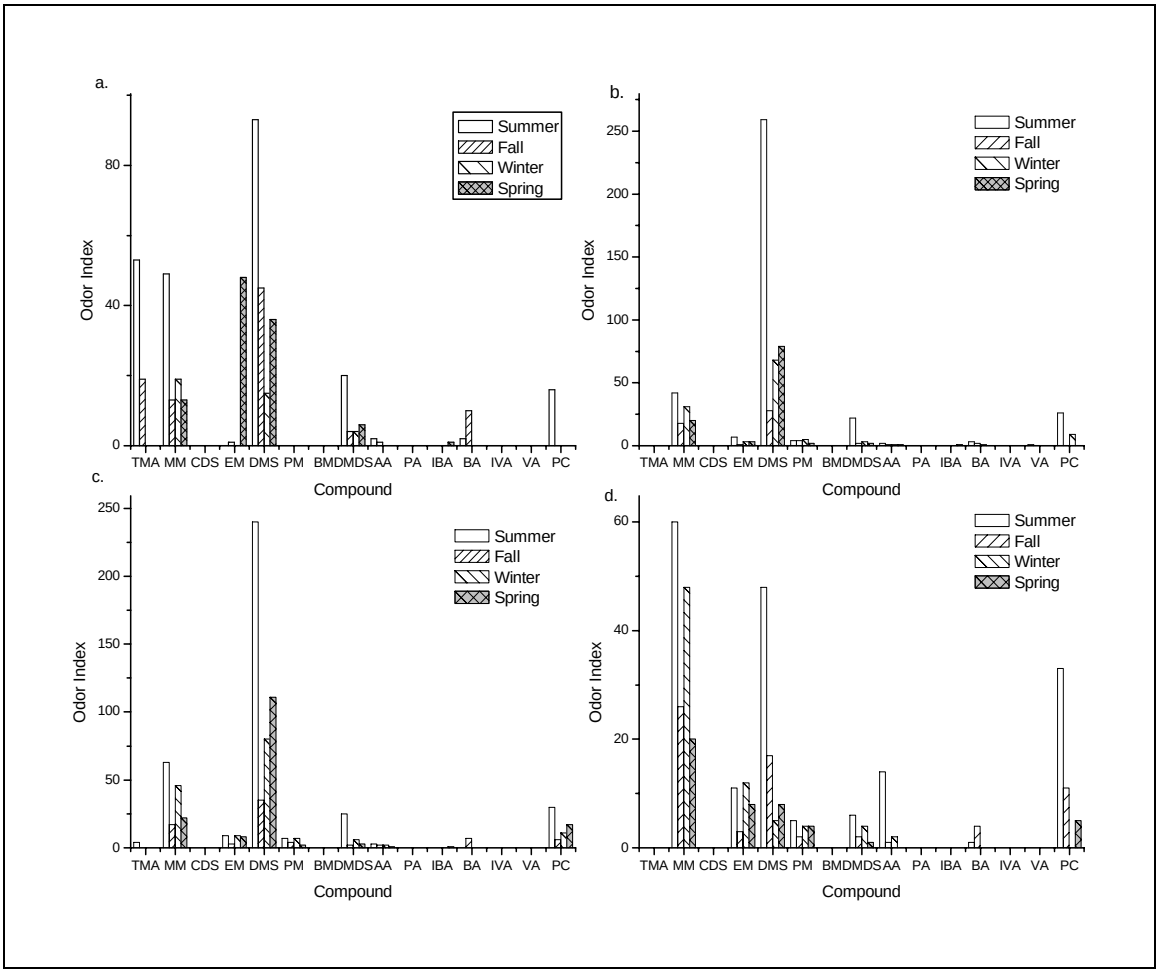


Figure 4.1: Odor index for each compound (all four seasons).

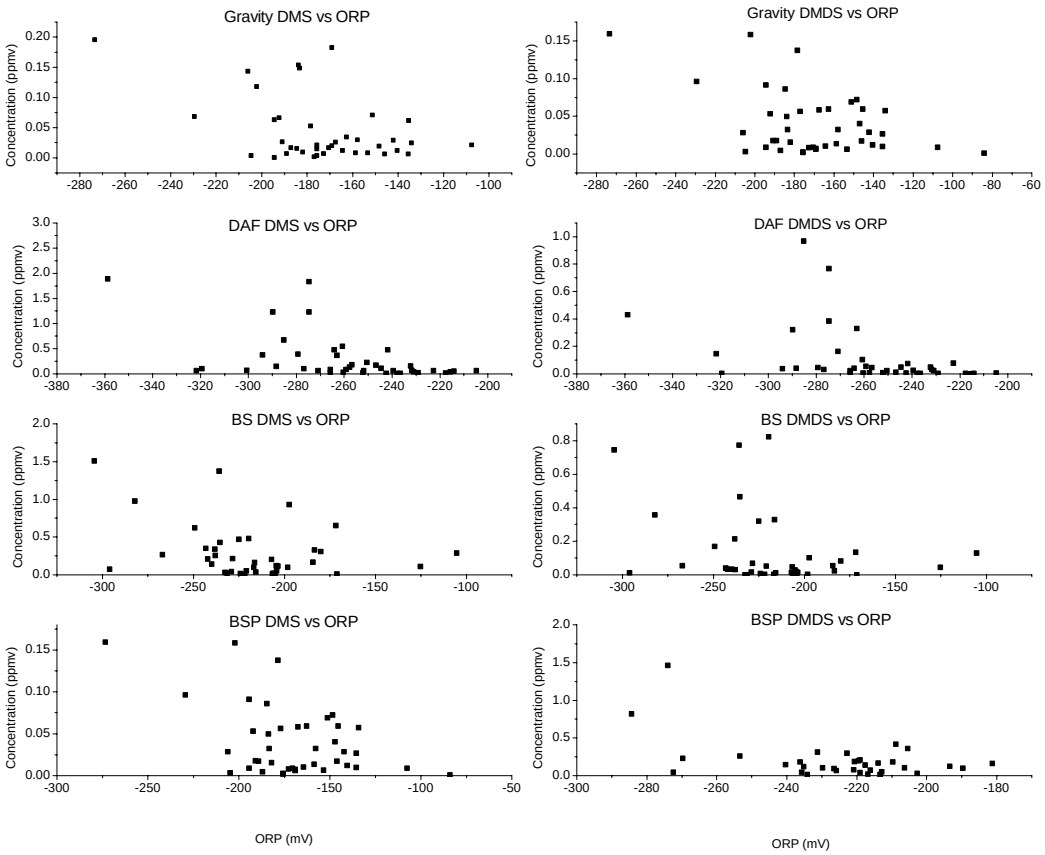
values of sludge, although the data is widely scattered (correlation coefficient R^2 = 0.6 to 0.69). Noticeably, at the ORP values of above –100 mV, where conditions become more oxidizing, sulfur compounds were seldom detected (Figure 4.3). This result indicates the on-site odor release of the solid handling processes could be controlled by increasing the ORP with the addition of an oxidant, and further investigation is desirable. In addition, research needs to be performed to compare how each odorant affects human perception

when accompanied by other known strong odorants. Table 4.4 shows the results for iron and calcium tests performed on the sludges. When graphed (not shown) versus the odorants released, points were too scattered to make any significant correlations, implying that there are other factors involved. In the future, correlations between several parameters and odorants released must also be performed.

Table 4.4: Average concentration of iron and calcium for each process.

Process		Fe (mg/L)	Ca (mg/L)
BS	Summer	2026	707
	Fall	1934	650
	Winter	8164	2498
	Spring	40229	11090
DAF	Summer	6660	1174
	Fall	2960	686
	Winter	11302	2113
	Spring	53721	9569
GR	Summer	718	732
	Fall	461	541
	Winter	2268	3036
	Spring	16319	14506
BSP	Summer	2349	747
	Fall	1686	531
	Winter	8987	2572
	Spring	42190	10678
DWL	Summer	38006	116987
	Fall	35214	111078
	Winter	37408	130112
	Spring	32158	90742

Figure 4.2: Sulfurs in blended and blended sludge with polymer, gravity, and DAF thickened sludge.



Although R^2 values were not all that great for the correlation graphs between ORP and the different reduced sulfurs, Table 4.5 shows that P values for each test were all less than 0.05 implying that these values are all either "highly" significant or "extremely" significant.

Table 4.5: Linear R^2 values and p values for correlation graphs in figure 4.2

Sludge Type	Value	DMS vs ORP	DMDS vs ORP
BSP	R^2	0.246	0.3301
	P	0.00285	0.00038
BS	R^2	0.1515	0.1375
	P	0.01432	0.02014
GR	R^2	0.2797	0.2182
	P	0.00064	0.00207
DAF	R^2	0.3398	0.3054
	P	< 0.0001	0.00032

Other than ORP, iron concentration in the sludge was also found to have a slight positive correlation with the amount of sulfur compounds released from sludge except limed dewatered cake; (data not shown). In the case of dewatered limed samples, the higher the iron concentration the lower the reduced sulfur concentrations in the headspace. As for the relation between iron content and odor production, correlations were not very clear and further investigation should be made.

Conclusion

In general, more odorants were released from the processes during the summer than any other season. Of the odorants detected from the samples, sulfur compounds, especially DMS and MM were identified as the most important. The ORP of the sludge was identified as a key parameter to control the release of odorants, at least sulfur compounds, from the solids handling processes, as suggested in the study of Kim et al. (2002). At higher ORP values, less release of odorants was observed; above an ORP of –100 mV, the release of the reduced sulfurs was diminished. The production of reduced sulfur compounds may be decreased by way of oxidant addition, although further investigation is required.

Iron addition, although not perfectly clear, appears to increase the release of odorous compound from sludges except the limed product, guaranteeing further investigation. Future studies for this project include the addition of different oxidants to the sludge to increase the ORP and continued monitoring of plant conditions and the odorant release.

Chapter 5: Future Research and Recommendations

Introduction

Measuring ORP is a simple parameter that can be performed manually or automatically in any wastewater treatment plant (WWTP) operation and can even be done continuously online. Using this parameter, one can predict type of odorants that will be released from the sludge. Because of the correlation found in past research, we conducted a small investigation on the effect of oxidant addition on sludge odors. Four different oxidants were tested; they include potassium ferrate (K_2FeO_4), sodium hypochlorite (NaOCl), calcium nitrate ($Ca(NO_3)_2$), and potassium permanganate (K_2MnO_4). All four oxidants have high oxidation potentials and fast reaction rates. Ferrate (VI) has the highest redox potential at 2.20 V. After ferrate, permanganate has the second highest at 1.679 V, then hypochlorite of 1.482 V and last calcium nitrate of 0.88 V (Jiang, 2002; LaGrega, 2001).

The amount of odors released from the wastewater process usually increases as the solid flows downstream to the thickening processes because of the development of more septic conditions. The sludge thickening processes are, therefore, the most important source of malodors (WEF, 1995; Kim, 2002).

Because of the release of these malodorous substances, wastewater sludge samples were collected from primary gravity thickeners and secondary dissolved air flotation thickeners. Eight 300 ml samples (of each type of sludge) were run simultaneously for a period of 24 hours and were analyzed for common odorants at every

four-hour time intervals. Each sample was placed in a 500 ml amber glass jar and a mixing blade was placed inside in order to provide constant mixing (Six Paddle Stirrer by Phips and Bird Inc. Richmond, VA) at 60 rpm (Fig. 5.1). Each chemical was added only once at the beginning of the 24 hour run in doses of 0.0, 0.3, 0.5, and 0.8 grams. Duplicates were run for each chemical dose tested. The mouth of the jar was kept covered with Parafilm in order to keep the moisture from escaping and the samples from drying. At each four-hour interval, ORP and pH were measured and 10 ml of each sample were collected with a syringe and placed in a 20 ml glass vial, capped, and analyzed for odors.

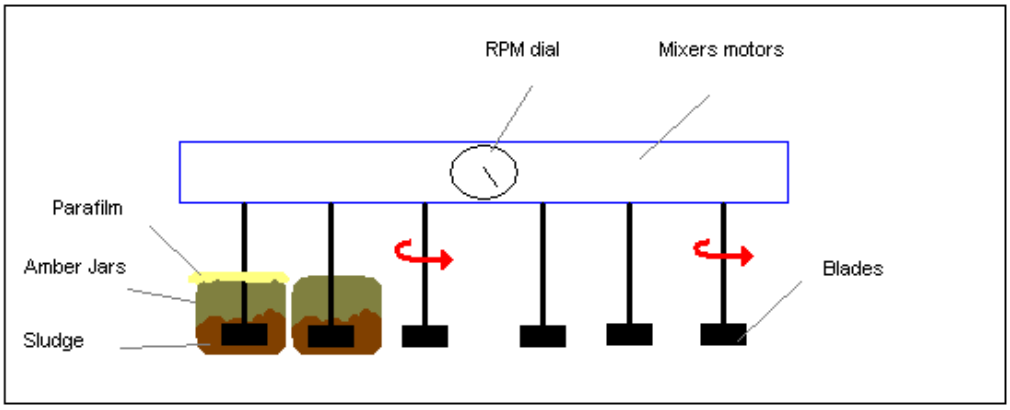


Figure 5.1: Experimental setup

Results

Although only one small dose was added at time zero, ORP of each sample quickly bounced back to its initial levels, but odor concentrations showed a definite correlation. The lower the ORP measured, the higher the reduced sulfurs concentrations found in the headspace. At ORP readings greater than -50 mV, almost all reduced sulfur compounds disappeared, and those that remained were all found at concentrations lower than the human olfactory thresholds. This study showed that the lower the ORP the higher the concentrations of odorants found in the gravity and the DAF thickened

sludges. This also follows the same trend found in our earlier results. Figure 5.2 shows the concentration profiles of dimethyl sulfide and methyl mercaptan according to the ORP of the sludge. These two compounds result more of a chemical oxidation reaction than a biologically mediated reaction and are therefore more likely to be influenced by the ORP conditions in the sludge. As the ORP began to return to its original state, or lower, the sulfurs also began increasing, thus showing that single doses of chemicals were not sufficient to completely remove the odor problem.

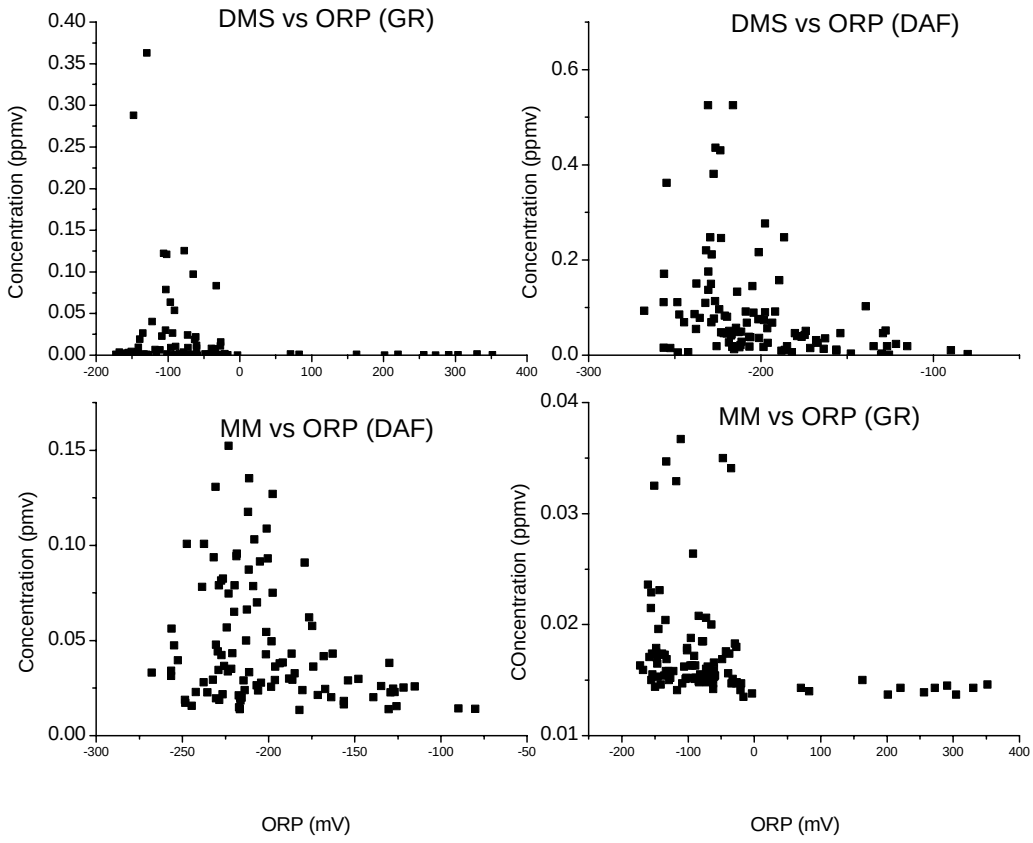


Figure 5.2: Methyl mercaptan and dimethyl sulfide concentrations plotted vs corresponding ORP values.

For the four different oxidants, for the decrease in methyl mercaptan odorant, the chemical that had the best results was calcium nitrate followed by potassium ferrate.

Calcium nitrate decreased odorant formation by the biggest amount except for at 4 hrs with the DAF thickened sludge.

For the formation of dimethyl sulfide, the chemical oxidant with the best results was potassium permangante, which had the biggest decrease at times 4 and 24 hours with the DAF thickened sludge and showed a decrease at all times with the gravity thickened sludge. The second oxidant with the best results was calcium nitrate, which also had a decrease in odorants at all times and the biggest decrease at time 4 hrs with the gravity thickened sludge.

Table 5.1 shows that although the graphs do not show a linear correlation, P values do fall within the significant range. This goes to show that there is a definite correlation between ORP and the sulfurs released although it also shows that there are other parameters that must play a role in the amount of odorants released.

Table 5.1: Linear R^2 values and P values for correlation graphs in figure 5.2

Sludge Type	Value	DMS vs ORP	MM vs ORP
GR	R^2	0.0202	0.0667
	P	0.15244	0.00852
DAF	R^2	0.12622	0.08481
	P	0.00023	0.00284

Conclusion

The results of this research have shown to go hand in hand with our original predictions. Measuring the ORP of the different wastewater sludge after and without the addition of chemical oxidants has shown that there is a definite correlation between the concentrations of reduced sulfurs released to the headspace and the fluctuations in ORP values. These are the same results that have been found in our past research and research done by others (Chang, 2002; Charpentier, 1998; Kim, 2002). Because dosing was low and not continuous, the release of odorants was not completely eliminated but only

retarded. For future research, a constant or intermittent feed of an oxidant and continuous monitoring the ORP profiles are recommended. Oxidants can change oxidation state of a sample condition to inhibit growth of sulfate reducing bacteria and promote growth of denitrifying bacteria, resulting in decreased production of reduced sulfurs. In addition, they oxidize reduced sulfur to sulfate. For the four different oxidants, with the two odorants compared, methyl mercaptan and dimethyl sulfide, the oxidant that had the best result on both odorants was calcium nitrate which showed good results at all times. For methyl mercaptan, the oxidant with the best result was calcium nitrate while for dimethyl sulfide the oxidant with the best result was potassium permangante. Monitoring ORP is easy and inexpensive and can be used as a parameter to limit the amounts of offensive odors released. Oxidation with potassium ferrate, sodium hypochlorite, calcium nitrate, and potassium permanganate, which are safer and easier to handle than the commonly used oxidants is recommended and is effective as long as the dosing is changed and the ORP is kept monitored.

Chapter 6: Conclusions

This work presents an improved method for the analysis of odorous compounds released from the thickening processes of a wastewater treatment. Our results indicate that the amount of reduced sulfur compounds released into the headspace increases with reducing conditions of the wastewater sludge with a strong correlation between the reduced sulfurs released and the sludge's Oxidation-Reduction Potential.. These reducing conditions can be easily monitored and improved within the process by means of changing sludge conditions. Sludge conditions can be improved via addition of a chemical oxidant.

Our method represent an improvement over the existing methods (Kim et al. (2002)), as it can separate and quantify 15 different chemical species within the sample. Because of the use of multidimensional GC-MS system, this method is able to diminish interference by other unwanted compounds which might affect the quantification of the compounds of interest. Another advantage of this method is that samples do not need to be analyzed in a lab under flow conditions, the fibers can be exposed in the field and without a source of flowing gas.

The Carboxen-PDMS fibers, used in our method, were able to pick up the amines, sulfurs, and mercaptans at concentrations that were lower than or comparable to the human odor thresholds for each of those compounds. Although the Volatile Fatty Acids were hardly detected, calibration curves showed that the polyacrylate fibers were also able to go as low as and comparable to the odor threshold for those chemicals. Standard curves for all compounds had R^2 values greater than 0.99 over the wide range of

concentration tested in this study. Past research has shown that the analytical procedures developed with SPME are linear over one order of magnitude and that detection limits can fall down to the low and even mid pptv level (Kim et al, 2002; Abalos et al, 1999, Pan et al, 1997). Our research also showed that the standard curves were linear for the concentrations tested. Methyl mercaptan was the only chemical for which a standard curve was not developed because of contamination issues coming from the permeation devices. It was suggested that oxidation of methyl mercaptan to dimethyl disulfide would occur on the fiber and therefore SPME could not be used to analyze this compound however past tests done on other methyl mercaptan permeation devices showed that methyl mercaptan had occurred without the presence of dimethyl disulfide. Future tests have to be performed on this highly reactive compound.

Although our standard curves were able to show good (linear) results, they were very time consuming and inefficient. For future research, it is recommended that the permeation rates of the devices be pre-chosen to fall within the range found in the samples so that all standards can be completed at once as opposed to one at a time. Although some of our devices did fall within the same range, others had permeation rates either too high or too low to conduct together and therefore delayed the production of standard curves. Permeation temperatures can also become a problem since most permeation devices are certified at different temperatures. Ensuring that all the permeation devices are certified at the same temperatures will cut down calibration time.

The one-year analysis of the odorants at all the sludge thickening processes showed a definite correlation between reduced sulfurs and the ORP measured. Research has shown in the past that release of reduced sulfurs is increased with negative ORP

values. After 15 years of ORP analysis, Charpentier et al (1998) found that the ORP threshold for the appearance of sulfides is from -250 to -300 mV. In this study, odorant concentrations were greatly reduced with ORP values greater than –100 mV. Although all processes had negative ORP values, the DAF thickened sludge had the lowest going below -300 mV, which correlates well with the highest concentrations of odorants, and the highest odor index values of all the processes.

Odor index values (odor concentration divided by odor threshold) were calculated to compare each compound with respect to its contribution with respect to human perception. Odor index comparisons showed that the chemical compounds which had the greatest impact on odors were methyl mercaptan and dimethyl sulfide for all the processes, trimethyl amine for the dewatered with lime, and para-cresol for the gravity thickened sludge. Dimethyl disulfide was found at all processes but was a lot lower in odor in comparison with the other compounds. The thickening processes, which showed the highest odor indexes, were the DAF thickened sludge and the Blended sludge which, showed odor index three times higher by comparison to the other thickening processes. These results follow those found by Kim et al (2002), showing the wastewater thickening processes as the processes, which release the highest concentrations of odorants.

Other parameters were also measured during this study but seemed to show little or no correlation. Although pH was measured weekly as well, it never varied by more than ± 0.6 and was very neutral for all the samples except for the gravity- thickened sludge, which had pH ranges from 5.69 to 7. Although iron is thought to have a positive impact on the release of sulfides, it showed a positive correlation in the sludges and a negative correlation with the dewatered limed cake, thus requiring further investigation.

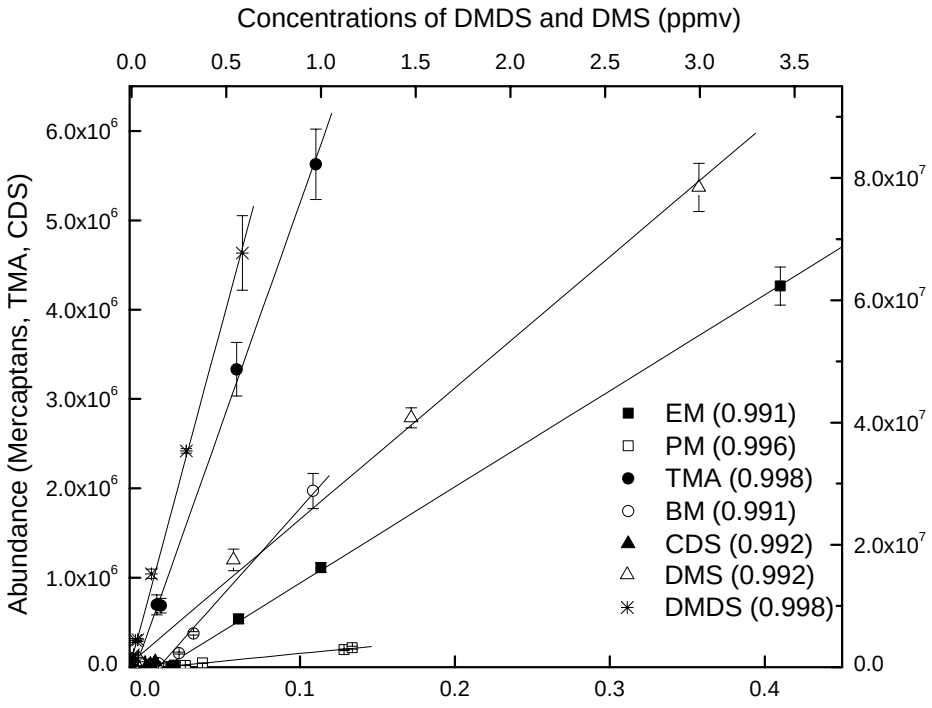
The oxidation study was initiated to investigate the relationship between ORP and odorant production. In this preliminary study four oxidants were added in order to increase the ORP of the tested sludge. The results of this research supported the correlation between ORP and reduced sulfur, but showed the difficulties in adding a highly reactive oxidant to a very reduced substance. Because the doses were not repeated and were very low, the results showed a highly fluctuating ORP that did not allow for good analysis of the results. Biosolids are very high in organic content and can therefore deplete the available oxidants very quickly (Neyens, 2003).

Appendix I

Calibration curves for all sulfurs, Amines, and Mercaptans

Concentration (ppmv)	Area	Flow (ml/min)	error	error amount	Limits
CDS					
0.0065	58189	442	0.04	2328	64008
0.0035	28773	815	0.07	2014	
0.0024	11960	1230	0.04	478	
0.0010	3064	3000	0.08	245	
0.0008	1737	3470	0.11	191	1563
DMS					
0.0025	172279	1100	0.11	18950	155051
0.0034	257388	805	0.07	18017	
0.0073	437298	380	0.15	65594	
0.0197	902742	140	0.14	126383	
0.0367	1491830	75	0.09	134264	
0.5382	17535865	395	0.1	1753586	
1.4764	40781958	144	0.04	1631278	
2.9943	78453184	71	0.05	3922659	86298502
DMDS					
0.5852	67734306	71	0.09	6096087	74507737
0.2885	35370783	144	0.01	353707	
0.1052	15258758	395	0.05	762937	
0.0335	4447802	1240	0.05	222390	
0.0223	4367794	70	0.07	305745	
0.0104	2027238	150	0.07	141906	
0.0052	1454010	300	0.11	159941	
0.0015	384474	1050	0.07	26913	
0.0004	81841	4010	0.07	5728	73656
TMA					
0.0075	697776	1100	0.16	111644	558220
0.0103	688798	805	0.12	82655	
0.0591	3331784	140	0.09	299860	
0.1103	5626446	75	0.07	393851	6751735
PM					
0.0102	4282	945	0.07	300	3426
0.0260	18995	370	0.09	1710	
0.0371	45071	260	0.05	2254	
0.1285	193932	75	0.05	9697	
0.1338	217246	72	0.07	15207	260695
BM					
0.0041	2192	1990	0.09	197	1973
0.0086	41623	945	0.07	2914	
0.0220	156469	370	0.07	10953	
0.0313	377058	260	0.05	18853	
0.1085	1972017	75	0.1	197202	2169219
EM					
0.0127	4801	2320	0.05	240	4321
0.0189	22056	1560	0.12	2646	
0.0603	538358	490	0.1	53835	
0.1136	1114469	260	0.05	55723	
0.4101	4265026	72	0.05	213251	4691529

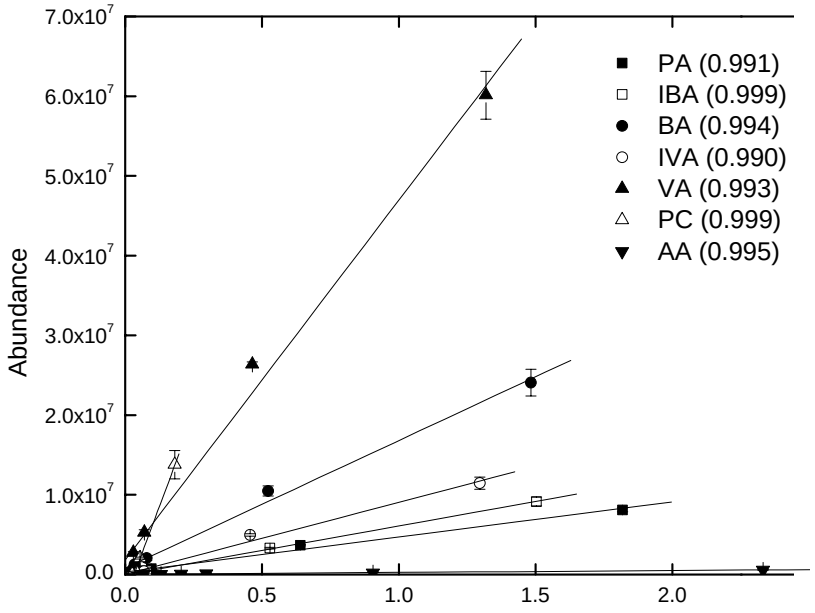
Calibration Curves for Sulfurs, Amines and Mercaptans



VFA calibration curves

Concentration (ppmv)	Area	Flow (ml/min)	error	error amount	limits
AA					
2.3309	568016	70	0.06	34081	624818
0.9065	247805	180	0.06	14868	
0.2967	114017	550	0.09	10262	
0.2040	94338	800	0.05	4717	
0.1316	54760	1240	0.12	6571	
0.0655	24875	2490	0.11	2736	22388
PA					
1.8180	8119438	74	0.03	243583	8931382
0.6406	3684154	210	0.02	73683	
0.0961	718740	1400	0.06	43124	
0.0420	472374	3200	0.05	23619	
0.0320	151089	4200	0.07	10576	120871
IBA					
1.5025	9139372	74	0.06	548362.33	10053309
0.5294	3307215	210	0.03	99216.438	
0.0794	462058	1400	0.05	23102.9	
0.0347	69387	3200	0.07	4857.104	
0.0265	103108	4200	0.07	7217.56	82486
BA					
1.4829	24083519	74	0.07	1685846	26491871
0.5226	10487322	210	0.06	629239	
0.0784	2056800	1400	0.15	308520	
0.0343	1267881	3200	0.05	63394	
0.0261	400658	4200	0.03	12020	320526
IVA					
1.2962	11462004	74	0.07	802340	12608204
0.4568	4961379	210	0.02	99228	
0.0685	407520	1400	0.07	28526	
0.0300	102995	3200	0.04	4120	
0.0228	149264	4200	0.06	8956	119411
VA					
1.3189	60123979	74	0.05	3006199	66136377
0.4648	26378440	210	0.07	1846491	
0.0697	5258676	1400	0.07	368107	
0.0305	2745297	3200	0.05	137265	
0.0232	754987	4200	0.05	37749	603990
PC					
2.0891	273149445	72	0.05	13657472	300464390
0.1812	13776934	830	0.13	1791001	
0.0543	2054717	2770	0.06	123283	
0.0435	221093	3460	0.02	4422	
0.0260	50943	5796	0.09	4585	40754

Calibration curves for all VFAs



Appendix II

Gravity sulfurs, amines and mercaptans plant data

DATE	MM (ppmv)	CDS (ppmv)	EM (ppmv)	DMS (ppmv)	PM (ppmv)	BM (ppmv)	DMDS (ppmv)
5/14/2003	0.0818	0.0014	0.0000	0.1958	0	0	0.1595
5/29/2003	0.0574	0.0014	0.0137	0.0682	0	0	0.0963
6/4/2003	0.0445	0.0012	0.0138	0.1177	0	0	0.1582
6/10/2003	0.0994	0.0010	0.0144	0.0526	0.0157	BDL	0.1376
6/18/2003	0.0459	0.0014	0.0143	0.1540	0	0	0.0496
6/25/2003	0.0666	0.0011	0.0139	0.0629	0.0119	BDL	0.0913
7/2/2003	0.0457	0.0011	0.0136	0.0153	0	0	0.0862
7/9/2003	0.0331	0.0040	0.0138	0.0065	0.0106	0	0.0175
7/16/2003	0.0804	0.0012	0.0144	0.1761	0.0123	0	0.0594
7/23/2003	0.0344	0.0011	0.0147	0.1489	0.0182	0	0.0326
7/30/2003	0.2260	0.0017	0.0147	0.1838	0.0160	0	0.0403
8/6/2003	0.1141	0.0013	0.0145	0.1432	0.0153	0	0.0285
8/20/2003	0.0189	0.0018	0.0136	0.1842	0	0	0.0010
9/4/2003	0.0203	0.0016	0.0000	0.0663	0	0	0.0533
9/16/2003	0.0222	0	0.0000	0.0245	0	0	0.0575
9/23/2003	0.0163	0.0017	0.0000	0.1824	0	0	0.0074
10/2/2003	0.0374	0.0034	0.0000	0.0708	0	0	0.0692
10/7/2003	0.0298	0.0016	0.0000	0.0258	0	0	0.0583
10/14/2003	0.0177	0.0018	0.0000	0.0192	0	0	0.0723
10/21/2003	0.0175	0.0017	0.0000	0.0621	0	0	0.0267
10/28/2003	0.0260	0.0012	0.0000	0.0216	0.0143	0	0.0089
11/4/2003	0.0557	0.0014	0.0000	0.0291	0	0	0.0289
11/18/2003	0.0294	0.0011	0.0137	0.0062	0	0	0.0098
11/25/2003	0.0289	0.0009	0.0137	0.0082	0.0112	0	0.0064
12/2/2003	0.0402	0.0011	0.0137	0.0119	0.0119	BDL	0.0123
12/18/2003	0.0158	0.0010	0.0000	0.0037	0	0	0.0020
12/23/2003	0.0338	0.0088	0.0000	0.0070	0	0	0.0176
12/30/2003	0.0309	0.0010	0.0164	0.0070	0.0000	0.0000	0.0082
1/6/2004	0.0543	0.0012	0.0140	0.0098	0.0120	0.0000	0.0155
1/13/2004	0.0268	0.0010	0.0141	0.0122	0.0116	0.0000	0.0104
1/20/2004	0.0381	0.0010	0.0141	0.0039	0.0110	BDL	0.0032
2/4/2004	0.1073	0.0021	0.0147	0.0017	0.0000	0.0000	0.0566
2/11/2004	0.0265	0.0019	0.0137	0.0167	0.0000	0.0000	0.0089
3/3/2004	0.0881	0.0033	0.0000	0.0216	0.0000	0.0000	0.2791
3/10/2004	0.0225	0.0014	0.0000	0.0201	0.0000	0.0000	0.0061
3/17/2004	0.0168	0.0015	0.0000	0.0150	0.0000	0.0000	0.0027
3/24/2004	0.0316	0.0013	0.0136	0.0007	0.0000	0.0000	0.0090
3/31/2004	0.0247	0.0014	0.0137	0.0263	0.0119	0.0000	0.0177
4/14/2004	0.0161	0.0012	0.0000	0.0165	0.0000	0.0000	0.0049
4/21/2004	0.0641	0.0014	0.0141	0.0345	0.0134	0.0000	0.0594
4/28/2004	0.0342	0.0010	0.0137	0.0083	0.0120	0.0000	0.0137
5/5/2004	0.0329	0.0012	0.0136	0.0301	0.0000	0.0000	0.0323

Gravity ORP and other parameters

DATE	pH	ORP	Fe	Calcium	CaCO3
1/6/04	6.18	-182	na	Na	Na
1/13/04	6.47	-164	Na	Na	Na
1/20/04	6.46	-205	Na	Na	Na
2/4/04	6.05	-177	Na	Na	Na
2/11/04	6.23	-171	Na	Na	Na
3/3/04	6.06	-176	Na	Na	Na
3/10/04	6.23	-169	Na	Na	Na
3/17/04	6.12	-176	Na	Na	Na
3/24/04	6.33	-194	Na	Na	Na
3/31/04	6.21	-191	Na	Na	Na
4/14/04	6.2	-187	Na	Na	Na
4/21/04	6.1	-163	Na	Na	Na
4/28/04	6.14	-159	Na	Na	Na
5/5/04	6.05	-158	Na	Na	Na
5/14/03	5.71	-273	639	784	0
5/29/03	5.92	-230	445	702	1.24
6/4/03	5.69	-202	746	876	1.38
6/10/03	5.98	-179	939	1118	1
6/18/03	5.96	-184	433	446	0.5
6/25/03	7.1	-194	352	285	0
7/2/03	6.62	-185	796	795	2.5
7/9/03	5.96	-146	866	834	0
7/16/03	6	-145	766	746	2.5
7/23/03	5.83	-183	889	849	0
7/30/03	5.87	-147	844	742	5
8/6/03	5.86	-206	839	812	0.25
8/20/03	5.71	-84	764	495	1.5
9/4/03	6.13	-192	469	443	0
9/16/03	5.83	-134	977	1056	3
9/23/03	5.88	-169	531	604	Na
10/2/03	5.89	-151	814	616	4.25
10/7/03	6.4	-168	803	725	4.875
10/14/03	6.17	-148	401	554	3.175
10/21/03	6.27	-135	454	491	3.75
10/28/03	6.17	-108	321	417	1.875
11/4/03	6.16	-142	444	544	5.75
11/18/03	6.22	-136	252	347	1.25
11/25/03	6.12	-153	309	547	0
12/2/03	6.21	-140	556	725	1
12/18/03	6.29	-176	Na	Na	1.625
12/23/03	6.3	-189	Na	Na	Na
12/30/03	6.22	-173	Na	Na	Na

Gravity VFAs plant data

DATE	AA (ppmv)	PA (ppmv)	IBA (ppmv)	BA (ppmv)	IVA (ppmv)	VA (ppmv)	PC (ppmv)
5/14/2003	1.8058	0.0973	0.0131	0.0056	0	BDL	0.0656
5/29/2003	0	0.0224	0	0.0243	BDL	0	0
6/4/2003	0	0.0416	0	0.0016	BDL	BDL	0.0619
6/10/2003	0.6888	0	0	0.0004	BDL	0	0.0609
6/18/2003	0.2444	0	0	0.0003	BDL	0	0.0606
6/25/2003	0.6940	0	0	0.0130	BDL	0	0.0607
7/2/2003	0.6710	0	0	0.0005	BDL	0	0.0602
7/9/2003	24.8170	0	0	0	BDL	0	0.0688
7/16/2003	0	0	0	0	0	0	0
7/23/2003	0.2572	BDL	0	0.0003	BDL	0	0.0607
7/30/2003	0.5201	0	0	0.0005	BDL	0	0.0632
8/6/2003	0.3770	0	0	0.0006	BDL	0	0.0603
8/20/2003	0	0	0	0	0	0	0
9/4/2003	0.1325	0	0	BDL	BDL	0	0
9/16/2003	0	0	0	0	0	0	0
9/23/2003	0	0	0.0227	0.0006	BDL	0	0.0611
10/2/2003	0.7273	0.0078	0.0223	0.0096	BDL	BDL	0.0654
10/7/2003	0	0	0.0167	0	0	0	0
10/14/2003	0.1855	0	0.0169	0	0	0	0.0601
10/21/2003	0.3687	0.0039	0.0181	0.0379	BDL	BDL	0.0601
10/28/2003	0	0	0	0	0	0	0
11/4/2003	0	0	0	0	0	0	0
11/18/2003	0	0	0	0.1237	0	0	0
11/25/2003	0.1530	0	0	0.0005	0	0	0
12/2/2003	0	0	0	0.0071	0	0	0
12/18/2003	0	0	0	0.0033	0	0	0
12/23/2003	0	0	0	0.0065	0	0	0
12/30/2003	0.4494	0	0	0	0	0	0
1/6/2004	0	0	0	0	0	0	0
1/13/2004	0.0619	0	0	0.0008	0	0	0
1/20/2004	0	0	0	0	0	0	0
2/4/2004	0	0	0	0	0	0	0
2/11/2004	0	0	0	0	0	0	0
3/3/2004	1.0912	0.0046	0.0236	0.0007	0	0	0
3/10/2004	0	0	0	0	0	0	0
3/17/2004	0	0	0	0	0	0	0
3/24/2004	0	0	0	0	0	0	0
3/31/2004	0.2398	0	0.0207	0	0	0	BDL
4/14/2004	0.2282	0	0	0	0	0	0
4/21/2004	0	0	0	0	0	0	0.0604
4/28/2004	0.1804	0	0	0	0	0	0
5/5/2004	0	0	0	0	0	0	0

Blended sludge sulfur, amines, and mercaptans plant data.

DATE	MM (ppmv)	CDS (ppmv)	EM (ppmv)	DMS (ppmv)	PM (ppmv)	BM (ppmv)	DMDS (ppmv)
5/14/2003	0.1007	0	0	1.5090	0	0	0.7439
5/29/2003	0.0403	0	BDL	0.9774	0.0122	0	0.3573
6/4/2003	0.0488	0.0016	BDL	0.1633	0	0	0.3299
6/10/2003	0.1087	0.0037	0	0.4785	0.0141	0	0.8223
6/18/2003	0.1188	0	0.0184	1.3727	0.0162	BDL	0.7726
6/25/2003	0.0631	0	0.0156	0.4303	BDL	0	0.4658
7/2/2003	0.0373	0.0139	0.0152	0.6213	0.0133	0	0.1684
7/9/2003	0.0339	0	0.0154	0.2645	0.0138	0	0.0536
7/16/2003	0.0294	0	BDL	0.3502	0	0	0.0405
7/23/2003	0.0458	BDL	BDL	0.4682	0.0117	0	0.3196
7/30/2003	0.2308	0.0017	0.0145	0.6537	0.0148	BDL	0.1341
8/6/2003	0.0855	0.0018	0	0.0742	0	0	0.0343
8/20/2003	0.0157	0.0015	0	0.0230	0	0	0.0069
9/4/2003	0.0182	0.0011	0.0146	0.1396	0.0114	0	0.0322
9/16/2003	0.0208	0	0	0.1087	0	0	0.0456
9/23/2003	0.0146	0	0	0.0153	0	0	0.0076
10/2/2003	0.0172	0.0015	0	0.0525	0	0	0.0510
10/7/2003	0.0164	0.0016	0	0.0367	0	0	0.0126
10/14/2003	0	0.0424	0	0.0423	0	BDL	0.0163
10/21/2003	0	BDL	0.0155864	0.0982	0	0	0.0022
10/28/2003	0.0154	BDL	0	0.0127	0.0127	0	0.0009
11/4/2003	0.0284	0	BDL	0.0729	0.0123	0	0.0118
11/18/2003	0.0152	0	BDL	0.0306	0	0	0.0010
11/25/2003	0.0147	0.0014	0	0.0201	BDL	0	0.0009
12/2/2003	0.0189	BDL	BDL	0.0497	BDL	BDL	0.0098
12/18/2003	0.0357	BDL	BDL	0.2150	0.0114	0	0.0673
12/23/2003	0.0485	BDL	0.0149	0.2569	0.0162	0	0.0308
12/30/2003	0.0321	BDL	0	0.2103	0.0179		0.0323
1/6/2004	0.0272	BDL	BDL	0.1664	0	0	0.0537
1/13/2004	0.0411	BDL	0.0153	0.1177	0.0241	0	0.0197
1/20/2004	0.0422	0.0011	0.0146	0.1169	0.0228	BDL	0.0143
2/4/2004	0.0369	0.0013	0.0000	0.0094	0	0	0.0471
2/11/2004	0.1080	0.0018	0.0147	0.2863	0	0	0.1296
3/3/2004	0.0692	0.0018	0.0151	0.3408	0	0	0.2145
3/10/2004	0.0504	0.0016	0.0000	0.3080	0	0	0.0812
3/17/2004	0.0157	BDL	0.0146	0.0980	0	0	0.0034
3/24/2004	0.0162	BDL	0.0000	0.0040	0.0139	0	0.0022
3/31/2004	0.0161	BDL	0.0163	0.2041	BDL	0	0.0130
4/14/2004	0.0159	BDL	0.0147	0.1100	0	0	0.0125
4/21/2004	0.0322	0.0011	BDL	0.9285	BDL	0	0.1003
4/28/2004	0.0252	BDL	0.0000	0.0133	0	0	0.0282
5/5/2004	0.0230	0.0013	0.0142	0.3296	BDL	0	0.0230

Blended sludge VFAs plant data

DATE	AA (ppmv)	PA (ppmv)	IBA (ppmv)	BA (ppmv)	IVA (ppmv)	VA (ppmv)	PC (ppmv)
5/14/2003	0.4894	0.0147	0	BDL	BDL	0	0.0697
5/29/2003	0.4078	0	0	0	0	0	0
6/4/2003	0.0849	0	0	BDL	BDL	0	0.0604
6/10/2003	0	0	0	0	BDL	0	0.0615
6/18/2003	0.3093	0	0	BDL	BDL	0	0.0994
6/25/2003	0.6123	0	0	BDL	BDL	0	0.0661
7/2/2003	0.5658	0	0	BDL	BDL	0	0.0620
7/9/2003	0.5104	0	0	BDL	BDL	0	0.0602
7/16/2003	0.5819	0	0	BDL	BDL	0	0
7/23/2003	0.2827	0	0	BDL	BDL	0	0.0605
7/30/2003	0.3731	0	0	0	BDL	0	0.0739
8/6/2003	0.3767	0	0	BDL	BDL	0	0.0601
8/20/2003	na	NA	na	NA	NA	NA	na
9/4/2003	na	NA	na	NA	NA	NA	na
9/16/2003	0	0	0	0	0	0	0
9/23/2003	0	0	0.0445	BDL	BDL	0	0.0618
10/2/2003	0.1455	0	0.0179	BDL	0	0	BDL
10/7/2003	0	0	0.0153	BDL	0	0	0
10/14/2003	0.1782	0	0.0185	0	0	0	0
10/21/2003	0.1170	0	0.0191	BDL	BDL	0	0.0602
10/28/2003	0	0	0	0	0	0	0
11/4/2003	0.1694	0	0	0	0	0	0
11/18/2003	0.7477	0	0	0	0	0	0
11/25/2003	0.1491	0	0	BDL	0	0	BDL
12/2/2003	0.7926	0	0	0	0	0	0
12/18/2003	1.3190	0	0	0.2050	0	0	0
12/23/2003	0	0	0	0	BDL	0	0
12/30/2003	0	0	0		0	0	0
1/6/2004	0	0	0	0	0	0	0
1/13/2004	0	0	0	0	0	0	BDL
1/20/2004	0	0	0	0	0	0	0.0601
2/4/2004	0.6161	0	0.0168	BDL	0	0	0.0603
2/11/2004	0	0	0	0	0	0	0
3/3/2004	1.0368	0	0.0236	BDL	0	0	0
3/10/2004	0.3507	0	0	0	0	0	0.0606
3/17/2004	0	0	0	0	0	0	0
3/24/2004	0	0	0	0	0	0	0
3/31/2004	0.2428	0	0.0219	0	0	0	0.0601
4/14/2004	0.3350	0	0.0489	0	0	0	0.0600
4/21/2004	0.2059	0	0	BDL	0	0	0.0701
4/28/2004	0.2302	0	0.0191	0	0	0	0
5/5/2004	0.1722	0	0	0	0	0	0

Blended sludge ORP and other parameters plant data

DATE	pH	ORP	Fe	Calcium
5/14/2003	6.52	-304.4	2134	763.29
5/29/2003	6.77	-282.1	2275	656.25
6/4/2003	6.8	-216.3	2396	711.875
6/10/2003	6.69	-219.6	2032	636
6/18/2003	6.5	-235.8	2038	642.25
6/25/2003	6.66	-235.3	1005	342.5
7/2/2003	7.76	-249.3	2589	892.875
7/9/2003	6.81	-266.9	2206	695.375
7/16/2003	6.93	-243.1	2673	786
7/23/2003	6.47	-224.9	2335	847.25
7/30/2003	6.48	-171.7	2320	893.875
8/6/2003	7.35	-401	1755	661.375
8/20/2003	6.41	-206.2	2190	703.75
9/4/2003	6.86	-240	421	665.75
9/16/2003	6.53	-125.3	1752	1040
9/23/2003	6.73	-224.2	1780	588.125
10/2/2003	7.08	-220.8	2062	586.625
10/7/2003	6.91	-215.8	1847	629.25
10/14/2003	6.87	-229.1	1462	518.875
10/21/2003	6.69	-198.2	2032	701.375
10/28/2003	6.52	-171	1838	818
11/4/2003	7.05	-296	1749	500.75
11/18/2003	6.73	-232.6	2447	698.875
11/25/2003	6.63	-231.4	2447	619.375
12/2/2003	6.62	-204.2	1941	571.6
12/18/2003	6.72	-228.4	1960	607.75
12/23/2003	6.69	-238	1825	574.5
12/30/2003	6.83	-242.2	2370	628.75
1/6/2004	6.72	-184.2	1106.1	513.225
1/13/2004	6.73	-204.5	1188.5	524.75
1/20/2004	6.7	-203.5	1411.5	543.5
2/4/2004	6.77	-206.5	1871.3	731.5
2/11/2004	6.66	-105.3	1098.9	741
3/3/2004	6.82	-238.1	48100	13800
3/10/2004	6.47	-180	33200	13200
3/17/2004	7	-216.8	51600	12600
3/24/2004	6.88	-221.7	48200	12100
3/31/2004	6.61	-207	33050	9880
4/14/2004	6.9	-203.9	39400	9570
4/21/2004	6.67	-197.3	46150	13000
4/28/2004	6.89	-205.1	na	11322
5/5/2004	6.58	-183.5	30000	7050

Blended sludge with polymer sulfurs, amines, and mercaptans plant data

DATE	MM (ppmv)	CDS (ppmv)	EM (ppmv)	DMS (ppmv)	PM (ppmv)	BM (ppmv)	DMDS (ppmv)
5/14/2003	0.1201	0	0	1.4612	0	0	0.7338
5/29/2003	0.0608	0	0.0147	0.8187	BDL	0	0.6409
6/4/2003	0.0429	0.0011	BDL	0.4198	0	0	0.1285
6/10/2003	0.0827	0.0018	0	0.1898	0	0	0.5134
6/18/2003	0.0714	0	BDL	0.0729	0.0014	BDL	0.2861
7/9/2003	0.1021	0	0	0.0450	BDL	0	0.3836
7/16/2003	0.0347	0.0011	BDL	0.2291	0.0017	0	0.1079
7/23/2003	0.0374	0	BDL	0.1961	0.0018	0	0.1235
7/30/2003	0.2095	0.0012	BDL	0.3616	0.0024	BDL	0.1811
8/20/2003	0.0189	0.0014	0	0.1837	0	0	0.0667
9/23/2003	0.0172	0.0015	0	0.0479	0	0	0.0723
10/2/2003	0.0263	0	0	0.1692	0	0	0.0876
10/7/2003	0.0174	0.0014	0	0.0678	0	0	0.0921
10/14/2003	0.0167	0.0012	0	0.0762	0	0	0.0656
10/21/2003	0.0161	BDL	0.0145	0.1478	0	0	0.0279
10/28/2003	0.0212	0.0010	BDL	0.1846	0.0014	0	0.0427
11/4/2003	0.0945	0.0012	0.0147	0.2590	0	0	0.2877
11/18/2003	0.0910	0.0009	0.0147	0.1205	BDL	BDL	0.0915
11/25/2003	0.0618	0.0010	0.0149	0.0952	BDL	0	0.1479
12/18/2003	0.0378	0.0011	0.0146	0.3139	BDL	0	0.1443
12/23/2003	0.1133	0.0011	0.0146	0.1395	0.0015	0	0.0741
12/30/2003	0.0664	0.0010	BDL	0.1026	0	0	0.0988
1/6/2004	0.0210	BDL	BDL	0.0400	0	0	0.0569
1/13/2004	0.0619	0.0009	BDL	0.0524	BDL	0	0.0741
1/20/2004	0.2277	0.0010	0.0149	0.1010	0.0022	0	0.0820
2/4/2004	0.1002	0.0019	0.0150	0.0321	0	0	0.1341
3/3/2004	0.1240	0.0015	0.0150	0.2956	0	0	0.2227
3/17/2004	0.0347	0.0011		0.0215	0	0	0.0561
3/24/2004	0.1207	0.0010		0.0140	0.0022	0	0.0443
3/31/2004	0.0541	BDL	0.0155	0.2111	0.0015	0	0.0696
4/14/2004	0.0269	0	0.0150	0.1032	BDL	0	0.0639
4/21/2004	0.0406	BDL	BDL	0.1251	BDL	0	0.1334
4/28/2004	0.0206	BDL		0.0174	0	0	0.0111
5/5/2004	0.0413	0.0014	0.0149	0.1605	0.0000	0	0.1225

Blended sludge with polymer VAFs plant data

DATE	AA (ppmv)	PA (ppmv)	IBA (ppmv)	BA (ppmv)	IVA (ppmv)	VA (ppmv)	PC (ppmv)
5/14/2003	1.0706	0.0337	0	BDL	0	0	0.0668
5/29/2003	0.6166	0	0	0	0	0	0
6/4/2003	0.0427	BDL	0	BDL	BDL	0	0.0612
6/10/2003	0	0	0	BDL	BDL	0	0.0610
6/18/2003	0.4773	0	0	BDL	BDL	0	0.1188
7/9/2003	0.2465	0	0	0.0275	BDL	0	0.0608
7/16/2003	0.6080	0	0	BDL	BDL	0	0
7/23/2003	0.1908	0	0	0	BDL	0	0.0601
7/30/2003	0.2702	0	0	0	BDL	0	0.0626
8/20/2003	na	NA	na	NA	NA	NA	na
9/23/2003	0	0	0.0266	BDL	BDL	0	BDL
10/2/2003	0.1587	0	0.0178	BDL	BDL	0	0
10/7/2003	0	0	0.0198	BDL	0	0	0
10/14/2003	0.1042	0	0	BDL	BDL	0	0
10/21/2003	0.1172	0	BDL	0	0	0	0
10/28/2003	0	0	0	0	0	0	0
11/4/2003	0.7521	0	0	BDL	BDL	0	0.0604
11/18/2003	0	0	0	0	0	0	0
11/25/2003	0.2255	0	0	BDL	0	0	0
12/18/2003	0	0	0	0	0	0	0
12/23/2003	0	0	0	0	0	0	0
12/30/2003	0	0	0	0	0	0	0
1/6/2004	0	0	0	0	0	0	0
1/13/2004	0.1909	0	0	0	0	0	0.0602
1/20/2004	0.0754	0	0	0	0	0	0
2/4/2004	0	0	0	0	0	0	0
3/3/2004	0	0	0	0	0	0	0
3/17/2004	0	0	0	0	0	0	0
3/24/2004	0	0	0.0202	BDL	0	0	0
3/31/2004	0.4083	0	0.0264	BDL	0	0	BDL
4/14/2004	0.3050	0	0	0	0	0	0
4/21/2004	0.3596	0	0	0	0	0	0
4/28/2004	0.1009	0	0.0166	0	0	0	0
5/5/2004	0.1827	0	0.0208	BDL	0	0	0

Blended sludge with polymer ORP and other plant data

DATE	pH	ORP	Fe	Calcium	CaCO3
5/14/2003	6.45	-274	2302	817.4	0
5/29/2003	6.73	-284.3	2343	687.5	1.245
6/4/2003	6.8	-208.8	2268	657.5	1.125
6/10/2003	6.71	-220.6	1880	583.875	10
6/18/2003	6.82	-216.2	2194	686.125	1.25
7/9/2003	6.75	-272.4	2700	858.125	0
7/16/2003	7.02	-269.7	2808	835	2
7/23/2003	6.53	-219.5	2175	777.375	0
7/30/2003	6.55	-205.5	2608	892.375	6.175
8/20/2003	6.63	-236.2	2217	673.375	2.5
9/23/2003	6.62	-235.7	1360	505.5	na
10/2/2003	7.04	-213.9	1980	591.25	10.25
10/7/2003	7.08	-225.8	1961	659.375	1.25
10/14/2003	6.88	-220.9	2200	773.5	1.25
10/21/2003	6.92	-240.3	1917	673.75	3.75
10/28/2003	6.87	-209.7	1249	428.875	2.5
11/4/2003	6.99	-253.4	1739	489.75	2.5
11/18/2003	6.95	-235.2	1184	375.3	4.5
11/25/2003	6.73	-226.5	1659	306.8	0
12/18/2003	6.79	-231.2	1831.5	555	0.5
12/23/2003	6.82	-217.6	1466	483.25	1.25
12/30/2003	6.87	-229.8	1604.8	427.275	32
1/6/2004	6.88	-219.1	1067.75	344.3	3.335
1/13/2004	6.73	-212.9	845.75	334.4	5.43
1/20/2004	6.75	-189.7	1430	564.25	6.18
2/4/2004	6.65	-202.8	1574.9	760	14.53
3/3/2004	6.92	-222.8	47400	13000	na
3/17/2004	7.01	-216.8	48700	12800	na
3/24/2004	6.99	-234.2	42100	11400	9900
3/31/2004	6.99	-219.1	32950	9670	7.5
4/14/2004	6.95	-206.4	38850	9930	9.45
4/21/2004	6.74	-193.4	53250	12500	4.15
4/28/2004	6.95	-213.3	29980	9345	6.7
5/5/2004	6.67	-181.3	49500	9100	na

DAF sulfurs, amines, and mercaptans plant data

DATE	MM (ppmv)	CDS (ppmv)	EM (ppmv)	DMS (ppmv)	PM (ppmv)	BM (ppmv)	DMDS (ppmv)
5/5/2004	0.0161	0	0.0613	0.0220	0	0	0.0082
5/14/2003	0.0473	0	0	1.8848	0	0	0.4309
5/29/2003	0.0575	0	0.0022	1.8331	0.0130	0	0.7682
6/4/2003	0.0549	0	0.0027	1.2259	0	0	0.3836
6/10/2003	0.0737	0.0033	0	0.6740	0.0193	0	0.9690
6/18/2003	0.0609	0.0010	BDL	0.0609	0	0	0.1649
6/25/2003	0.0611	0	0.0061	1.2295	0.0115	BDL	0.3216
7/2/2003	0.0308	0	0.0063	0.1815	0	0	0.0457
7/9/2003	0.0211	0.0029	0	0.3933	0.0151	0	0.0472
7/16/2003	0.0253	0	0.0021	0.3798	0	0	0.0372
7/23/2003	0.0540	0	0.0020	0.3686	0	0	0.3291
7/30/2003	0.1305	0.0011	BDL	0.0657	0.0123	BDL	0.1474
8/6/2003	0.0283	0	0	0.0679	0	0	BDL
8/20/2003	0.0151	0.0010	BDL	0.1744	0	0	0.0111
9/4/2003	0.0166	0	0.0026	0.1483	BDL	0	0.0416
9/23/2003	0	0.0010	0	0.0120	0	0	0.0039
10/2/2003	0.0171	0.0021	0	0.0845	0	0	0.0553
10/7/2003	0.0156	0.0010	0	0.0275	0	0	0.0056
10/14/2003	0.0148	0.0010	0.0028	0.1335	0	0	0.0100
10/21/2003	0	BDL	BDL	0.0602	0	0	0.0023
10/28/2003	0.0154	0.0009	BDL	0.0533	0.0115	0	0.0017
11/4/2003	0.0181	0.0013	0	0.0985	0	0	0.0041
11/18/2003	0.0152	0.0009	0	0.0089	0	0	0.0030
11/25/2003	0.0254	0.0017	0	0.0364	BDL	0	0.0229
12/2/2003	0.0396	0.0011	0	0.0989	0.0128	BDL	0.0328
12/18/2003	0.0340	0.0010	0.0022	0.0608	0.0123	0	0.0770
12/23/2003	0.0417	0.0010	0.0026	0.0643	0.0140	0	0.0265
12/30/2003	0.0215	0.0009	0.0021	0.0866	0	0	0.0227
1/6/2004	0.0574	0	0.0037	0.0672	0.0149	0	0.0314
1/13/2004	0.0510	0.0009	0.0026	0.1102	0.0231	0	0.0493
1/20/2004	0.0208	0.0009	BDL	0.0260	BDL	0	0.0027
2/4/2004	0.0230	0.0012	0	0.0056	0	0	0.0027
2/11/2004	0.0316	0.0015	0.0042	0.2267	0	0	0.0241
3/3/2004	0.0364	0.0013	0.0040	0.5446	0	0	0.1045
3/10/2004	0.0414	0.0012	0.0046	0.4796	0	0	0.0733
3/17/2004	0.0149	0.0010	0.0037	0.0385	0	0	0.0006
2/24/2004	0.0214	0.0009	0	0.0040	0.0116	0	0.0067
3/31/2004	0.0197	0	0.0066	0.4798	0	0	0.0390
4/14/2004	0.0158	0	0.0034	0.0623	0	0	0.0044
4/21/2004	0.0264	0	0.0050	0.1588	BDL	0	0.0482
4/28/2004	0.0169	0	0	0.0081	0	0	0.0032

DAF VFAs plant data

DATE	AA (ppmv)	PA (ppmv)	IBA (ppmv)	BA (ppmv)	IVA (ppmv)	VA (ppmv)	PC (ppmv)
5/5/2004	0	0	0	0	0	0	0
5/14/2003	0.4651	0	0	0	0	0	0.0623
5/29/2003	0	0.0370	0.0147	0.0300	0.0101	0.0514	0.0611
6/4/2003	0	0	0	0	0	0	0.0629
6/10/2003	0.1638	0	0	BDL	BDL	0	0.0614
6/18/2003	0.3893	0	0	BDL	BDL	0	0.2661
6/25/2003	0.4739	0	0	0.0299	BDL	0	0.0631
7/2/2003	0.3981	0	0	0	BDL	0	0.0601
7/9/2003	0.2252	0	0	BDL	BDL	0	0
7/16/2003	0.3912	0	0	0.0504	0.0044	0	0
7/23/2003	0.3444	BDL	0	0.0011	0.0035	0	BDL
7/30/2003	0.3157	0	0	BDL	BDL	0	BDL
8/6/2003	0	0	0	0	0	0	0
8/20/2003	0	0	0	0	0	0	0
9/4/2003	0.2401	0	0	0	0	0	0
9/23/2003	0.0991	0	0.0148	0.0051	0.0036	0	0
10/2/2003	0.1841	0	0.0193	0.0016	BDL	0	0
10/7/2003	0.2762	0	0.0212	0.0033	BDL	0	0
10/14/2003	0.1292	0	0.0151	0	0	0	0
10/21/2003	0.1084	0	0.0110	0	0	0	0
10/28/2003	0.3243	0	0	0.0590	BDL	0	0
11/4/2003	0	0	0	0	0	0	0
11/18/2003	0	0	0	0	0	0	0
11/25/2003	0.2659	0	0	0.0015	0	0	0
12/2/2003	0	0	0	0	0	0	0
12/18/2003	0	0	0	0.0098	0	0	0
12/23/2003	0	0	0	0	0	0	0
12/30/2003	0	0	0	0	0	0	0.0607
1/6/2004	0	0	0	0	0	0	0
1/13/2004	0	0	0	0	0	0	0
1/20/2004	0.0744	0	BDL	0	0	0	0
2/4/2004	1.0242	0	0.0194	0.0144	0.0045	0	0
2/11/2004	0	0	0	0	0	0	0.0601
3/3/2004	0	0	0	0	0	0	0
3/10/2004	0	0	0	0	0	0	0
3/17/2004	BDL	0	0	0	0	0	BDL
2/24/2004	0	0	0	0	0	0	0
3/31/2004	0.1805	0	0.0171	0	0	0	0
4/14/2004	0.3721	0	0.0213	BDL	0	0	0
4/21/2004	0.2286	0	0.0174	0	0	0	0
4/28/2004	0.3206	0	0.0227	0.0022	0	0	0

DAF ORP and other process parameters plant data

DATE	pH	ORP	Fe	Calcium
5/5/2004	7.31	-252.2	57000	6750
5/14/2003	6.88	-358.8	2798	666.6
5/29/2003	7.08	-274.8	3481	673.375
6/4/2003	6.93	-274.8	2877	597.5
6/10/2003	6.9	-285.2	2608	1153.5
6/18/2003	7.03	-270.9	2739	606
6/25/2003	7.12	-289.9	1285	287.5
7/2/2003	7.82	-256.8	3808	872
7/9/2003	7.09	-279.3	4070	886.25
7/16/2003	7.24	-294.2	4160	886.25
7/23/2003	7.05	-263	4401	1070.375
7/30/2003	6.95	-321.8	4003	1051.75
8/6/2003	7.04	-300.7	3189	698.5
8/20/2003	6.98	-246.7	2841	678.375
9/4/2003	7.25	-288.4	637	737.25
9/23/2003	7.17	-217.7	3331	770.125
10/2/2003	7.55	-259.2	2522	568.75
10/7/2003	7.55	-260.4	2885	696.625
10/14/2003	7.15	-257.7	3138	866.25
10/21/2003	7.14	-251.8	2785	776.875
10/28/2003	7.06	-214.1	2828	718.75
11/4/2003	7.24	-319.4	2794	647.125
11/18/2003	7.11	-265.9	3054	574.75
11/25/2003	7.09	-230.9	3420	705.625
12/2/2003	7.18	-276.9	2616	500.7
12/18/2003	7.03	-222.8	3073	687
12/23/2003	7.13	-239.5	3072.5	718.5
12/30/2003	7.17	-265.8	3059	557.75
1/6/2004	7.16	-231.8	1670.4	562
1/13/2004	7.05	-244.6	2736	694.75
1/20/2004	7.03	-229.1	2042.2	580.5
2/4/2004	7.2	-236.5	2297	508.45
2/11/2004	7.28	-250.6	2706	490.45
3/3/2004	7.3	-260.8	64600	11400
3/10/2004	6.83	-241.8	62400	10600
3/17/2004	7.12	-215.7	66400	12100
2/24/2004	7.34	-242.4	58200	10600
3/31/2004	7.26	-264.2	26300	5165
4/14/2004	7.08	-204.8	47750	8580
4/21/2004	7.23	-232.3	72700	10450
4/28/2004	7.33	-237.8	42300	9487

Dewatered cake sulfurs, amines, and mercaptans plant data

DATE	MM (ppmv)	CDS (ppmv)	EM (ppmv)	DMS (ppmv)	PM (ppmv)	BM (ppmv)	DMDS (ppmv)
5/29/2003	0.0360	0.0009	0.0146	0.4282	0.0190	0	0.2260
6/4/2003	0.0467	0	0.0154	0.5931	BDL	0	0.4598
6/10/2003	0.0461	0	0	0.1812	0	0	0.3863
6/18/2003	0.0477	0.0012	0.0151	0.9682	0	0	0.3024
6/25/2003	0.0873	0.0011	0.0155	0.6332	0	0	0.2560
7/2/2003	0.0402	0.0011	BDL	0.0745	0	0	0.2859
7/9/2003	0.0504	0.0013	BDL	0.3343	0	0	0.2930
7/16/2003	0.0789	0	0	0.2719	0	0	0.3606
7/23/2003	0.0523	0.0015	0	0.2088	0	0	0.0868
7/30/2003	0.1033	0.0241	0	0.2362	0	BDL	0.0438
8/6/2003	0.0492	0.0013	BDL	0.1541	0	0	0.0481
8/20/2003	0.0258	0.0051	0	0.3229	0	0	0.1946
9/4/2003	0.0345	0.0022	BDL	0.1458	0	0	0.2409
9/23/2003	0.0325	0.0030	0	0.3338	0	0	0.4924
10/2/2003	0.0289	0.0036	0	0.1700	0	0	0.3841
10/7/2003	0.0690	0.0021	0	0.0969	0	0	0.3740
10/14/2003	BDL	0.0023	0	0.2634	0	0	0.1573
10/21/2003	0.0145	0.0014	0	0.3336	BDL	0	0.2721
10/28/2003	0.0565	0.0022	0	0.3728	0	0	0.4081
11/4/2003	0.0721	0.0021	0	0.2184	0	0	0.3849
11/18/2003	0.0808	0.0014	0	0.0644	0	0	0.0534
11/25/2003	0.0707	0.0011	0.0148	0.1450	0	0	0.1901
12/18/2003	0.0344	0.0028	BDL	0.1670	0	0	0.2105
12/23/2003	0.0640	0.0015	BDL	0.1914	0	0	0.0574
12/30/2003	0.0656	0.0020	BDL	0.0748	BDL	BDL	0.1852
6/4/2004	0.0644	0.0017	0.0145	0.0850	0	0	0.0865
1/13/2004	0.0371	0.0021	BDL	0.0508	0	0	0.0445
1/20/2004	0.0811	0.0015	0.0150	0.0771	0.0161	BDL	0.0328
2/4/2004	0.0958	0.0105		0.0427	0	0	0.1270
3/3/2004	0.0419	0.0032		0.1910	0	0	0.1589
3/17/2004	0.0269	0.0021	BDL	0.2013	0	0	0.1076
3/24/2004	0.0702	0.0017	BDL	0.0059	0	0	0.2051
3/31/2004	0.0253	0.0016	0.0149	0.3049	0.0167	0	0.1741
4/14/2004	0.0235	0.0034	BDL	0.1252	0	0	0.3361
4/21/2004	0.0400	0.0031	0	0.1994	0	0	0.2399
4/28/2004	na	na	na	na	Na	na	na
5/5/2004	0.0219	0.0032	0	0.1380	0	0	0.1261

Dewatered cake VFAs plant data

DATE	AA (ppmv)	PA (ppmv)	IBA (ppmv)	BA (ppmv)	IVA (ppmv)	VA (ppmv)	PC (ppmv)
5/29/2003	0	0.0301	0	0.1213	BDL	BDL	0.0609
6/4/2003	0	0	0	BDL	BDL	0	0.0624
6/10/2003	0.4309	0.0393	BDL	BDL	BDL	BDL	0.0668
6/18/2003	0.2924	0.0299	0	BDL	0.0038	BDL	0.2422
6/25/2003	0.2862	0	0	BDL	BDL	0	0.0764
7/2/2003	0.3410	0	0	BDL	BDL	0	0.0615
7/9/2003	0.4320	0	0	BDL	BDL	0	0.0627
7/16/2003	0.2213	0	0	BDL	0.0017	0	BDL
7/23/2003	0.0638	0	0	BDL	0.0028	0	0.0622
7/30/2003	0	0	0	0	0	0	0
8/6/2003	0.3663	0	0	0	BDL	0	0.0624
8/20/2003	0	0	0	0	0	0	0
9/4/2003	0.2098	0	0	BDL	BDL	0	0
9/23/2003	0.1435	0	BDL	BDL	BDL	0	0.0605
10/2/2003	0.2958	BDL	0.0162	BDL	BDL	BDL	BDL
10/7/2003	0	0	0.0133	BDL	0	0	BDL
10/14/2003	0.2770	0	0.0127	0	0	0	BDL
10/21/2003	0.1382	0	0.0208	BDL	0	0	0
10/28/2003	0	0	0	0	0	0	0
11/4/2003	0.2666	0	0	0	0	0	BDL
11/18/2003	0	0	0	0	0	0	0
11/25/2003	0.7491	0	0	BDL	0	0	BDL
12/18/2003	0	0	0	0	0	0	0
12/23/2003	0.5878	0	0	0	0	0	0
12/30/2003	0	0	0	0	0	0	0
6/4/2004	0	0	0	0	0	0	0
1/13/2004	0.0713	0	0	BDL	0	0	BDL
1/20/2004	0.7193	0.0079	0.0134	BDL	0	BDL	BDL
2/4/2004	0	0	0	0	0	0	0.0610
3/3/2004	0.4213	0	0.0182	0	0	0	0
3/17/2004	0	0	0	0	0	0	0
3/24/2004	0.1145	0	0	0	0	0	0
3/31/2004	0.7090	0	0.0205	BDL	0	0	BDL
4/14/2004	0.1207	0	0	0	0	0	0
4/21/2004	0.2732	0	0	0	0	0	
4/28/2004	0.4349	0	0.0237	0	0	0	BDL
5/5/2004	0.0877	0	0.0254	0	0	0	BDL

Dewatered limed cake sulfurs, amines, and mercaptans plant data

DATE	TMA (ppmv)	MM (ppmv)	CDS (ppmv)	EM (ppmv)	DMS (ppmv)	PM (ppmv)	BM (ppmv)	DMDS (ppmv)
5/14/2003	0.1904	0.0668	0	0	0.3292	0	0	0.4326
5/29/2003	0.1165	0.0175	0.0027	0	0.3537	0	0	0.1584
6/4/2003	0	0.0679	0	0	0.5101	0	0	0.5915
6/10/2003	0.1505	0.0739	0	0	0.0998	0	BDL	0.3970
6/18/2003	0.0677	0.0275	0.0016	BDL	0.5585	0	0	0.3054
6/25/2003	0.0658	0.0381	0.0014	BDL	0.2586	0	0	0.1864
7/2/2003	0.4552	0.0503	0	0	0.0395	0	0	0.2344
7/9/2003	0.2207	0.0700	0.0018	BDL	0.1221	0	0	0.2096
7/16/2003	0.0842	0.0302	0.0013	BDL	0.0911	0	0.0120	0.1508
7/23/2003	0.1291	0.0578	0.0020	0	0.0792	0	0	0.2343
7/30/2003	0.0444	0.1468	0.0019	0	0.1242	0	0	0.1500
8/6/2003	0.0616	0.0739	0.0028	0	0.0070	0	0	0.1478
8/20/2003	0.0900	0.0151	0.0054	0	0.1886	0	0	0.0825
9/4/2003	0.0590	0.0204	0.0069	0	0.1656	0	0	0.1161
9/23/2003	0.0887	0	0.0084	0	0.1808	0	0	0.0940
10/2/2003	0.0835	0	0.0047	0	0.0889	0	0	0.0407
10/7/2003	0.1149	0.0154	0.0056	0	0.0642	0	0	0.0727
10/14/2003	0.0338	0.0154	0.0073	0	0.0970	0	0	0.1008
10/21/2003	0.0670	0.0156	0.0066	0	0.1579	0	0	0.0676
10/28/2003	0.0667	0.0168	0.0062	0	0.1887	0	0	0.0566
11/4/2003	0.0295	0.0200	0.0056	0	0.0554	0	0	0.0440
11/18/2003	0.0148	0.0191	0.0038	0	0.0461	0	0	0.0325
11/25/2003	0.0254	0.0159	0.0027	0.1321	0.0689	0	0	0.0248
12/18/2003	0.0161	0.0165	0.0055	0	0.0784	0	0	0.0333
12/23/2003	0.0340	0.0173	0.0032	0	0.0798	0	0	0.0316
12/30/2003	0.0756	0.0199	0.0030	BDL	0.0364	0	BDL	0.0378
1/6/2004	0.0278	0.0160	0.0028	0	0.0294	0	0	0.0176
1/13/2004	0.0253	0.0148	0.0033	0	0.0223	0	0	0.0190
1/20/2004	0	BDL	0.0658	0	0.0604	0	0	0.0139
2/4/2004	0.0878	0.0318	0.0114	BDL	0.0165	0	0	0.1363
3/17/2004	0.0601	0.0153	0.0079	0.3612	0.1297	0	0	0.0750
3/24/2004	0.0438	0.0155	0.0054	0	0.0010	0	0	0.0607
3/31/2004	0.0615	0.0173	0.0065	0	0.1333	0	0	0.0862
4/14/2004	0.0155	BDL	0.0086	0	0.0489	0	0	0.0615
4/21/2004	0.0785	0.0221	0.0038	0	0.1094	0	0	0.1276
4/28/2004	0.0630	0	0.0029	0	0.0718	0	0	0.0876
5/5/2004	0.0291	0.0151	0.0050	0	0.0651	0	0	0.0601

Dewatered limed cake VFAs plant data

DATE	AA (ppmv)	PA (ppmv)	IBA (ppmv)	BA (ppmv)	IVA (ppmv)	VA (ppmv)	PC (ppmv)
5/14/2003	0.1132	BDL	0	BDL	0	BDL	BDL
5/29/2003	BDL	0	BDL	0	0	BDL	0
6/4/2003	0	0	0	BDL	0.0216	BDL	0.0643
6/10/2003	0.2316	0	0	BDL	BDL	0	0.0605
6/18/2003	0	0	0	0	0	0	0
6/25/2003	0.5776	0	0	BDL	BDL	0	0.0613
7/2/2003	0.3730	0	0	0.0490	BDL	0	0.0605
7/9/2003	0.4645	0	0	BDL	0.0279	0	BDL
7/16/2003	0	0	0	0	0	0	0
7/23/2003	0.7586	0	0	BDL	BDL	0	0.0606
7/30/2003	0.3588	0	0	0	BDL	0	BDL
8/6/2003	0.2849	0	0	BDL	BDL	0	BDL
8/20/2003	0	0	0	0	0	0	0
9/4/2003	0.2271	0	0	BDL	BDL	0	0
9/23/2003	0.1538	0	BDL	0	0	0	BDL
10/2/2003	0	0	0	BDL	0	0	BDL
10/7/2003	0.1694	0	BDL	BDL	BDL	BDL	BDL
10/14/2003	0.2787	0	BDL	0	BDL	BDL	BDL
10/21/2003	0.2989	0	BDL	0.1782	BDL	BDL	BDL
10/28/2003	0	0	0	0	0	0	0
11/4/2003	0	0	0	0	0	0	0
11/18/2003	0	0	0	0	0	0	0
11/25/2003	0.3173	0	0	BDL	0	0	BDL
12/18/2003	0	0	0	0.1224	0	0	0
12/23/2003	0	0	0	0	0	0	0
12/30/2003	0	0	0	0	0	0	0
1/6/2004	0	0	0	0	0	0	0
1/13/2004	0	0	0	0	0	0	0
1/20/2004	0.0713	0	0	BDL	0	0	0
2/4/2004	0	0	0	0	0	0	0
3/17/2004	0	0	0	0	0	0	0
3/24/2004	0	0	0	0	0	0	0
3/31/2004	0.1937	0	0.0189	BDL	0	0	0
4/14/2004	0.1711	0	0	0	0	0	0
4/21/2004	0	0	0.0173	0	0	0	BDL
4/28/2004	0	0	0.0252	0	0	0	0
5/5/2004	0.1390	0	0.0235	0	0	0	0

Dewatered limed cake ORP and other parameters plant data

DATE	Fe	Calcium	CaCO3
5/14/2003	38344	119619.55	11.125
5/29/2003	38287	122659.1	14.63
6/4/2003	41199	107301.9	13.755
6/10/2003	36131	107243.48	16.25
6/18/2003	35158	107789.6	15
6/25/2003	34826	116726.05	10
7/2/2003	38291	107923.95	5.625
7/9/2003	39295	112292.95	10.375
7/16/2003	39804	130251.3	7.5
7/23/2003	35569	95456.615	9.5
7/30/2003	38754	145855.45	10
8/6/2003	na	125535.2	12.75
8/20/2003	39284	107767.05	17.5
9/4/2003	39138	131389.8	7.875
9/23/2003	39513	114833.45	na
10/2/2003	39118	108911.25	10.25
10/7/2003	37351	119138.15	10
10/14/2003	29409	113147.63	15.5
10/21/2003	35024	111029.35	11.25
10/28/2003	10315	36383.55	8.875
11/4/2003	39899	112638.4	13.75
11/18/2003	42525	139148.4	12.375
11/25/2003	41419	116732.5	0
12/18/2003	35683.38	132865.4	12.75
12/23/2003	37101.005	117029.2	15.75
12/30/2003	43839.33	114250	24.77
1/6/2004	44351.59	138551.6	23.835
1/13/2004	31738.575	146008.55	29.365
1/20/2004	32903.64	130686.1	19.23
2/4/2004	34208.33	121061.35	24.39
3/17/2004	43600	116000	230000
3/24/2004	35400	102000	228600
3/31/2004	29650	83050	8.95
4/14/2004	33100	100500	na
4/21/2004	35200	99900	13
4/28/2004	na	na	na
5/5/2004	16000	43000	2.65

Appendix III

Potassium Permanganate (DAF) oxidation results

CONTROL **TIME (hrs)**

	0	3	6	9	12	15	18	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0156	0.0188	0.0196	0.0479	0.0442	0.0337	0.0185	0.0333
CDS	0.0009	0.0010	0.0009	0.0010	0.0009	0.0012	0.0009	0.0011
DMS	0.0691	0.1112	0.1759	0.1375	0.2477	0.4307	0.5253	1.7824
DMDS	0.0228	0.9434	0.0839	2.1129	0.0990	0.2768	0.0841	0.3560

0.3 g **TIME (hrs)**

	0	3	6	9	12	15	18	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0218	0.0332	0.0563	0.0314	0.0341	0.0474	0.0544	0.0294
CDS	0.0010	0.0013	0.0015	0.0011	0.0011	0.0012	0.0013	0.0013
DMS	0.1134	0.0935	0.1708	0.1111	0.0153	0.3625	0.2166	0.1095
DMDS	0.4499	0.7248	1.3618	0.7041	0.2496	1.4638	0.8318	0.4370

0.5 g **TIME (hrs)**

	0	3	6	9	12	15	18	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0202	0.0279	0.0239	0.0785	0.0237	0.0351	0.0569	0.0281
CDS	0.0013	0.0011	0.0011	0.0009	0.0010	0.0012	0.0013	0.0013
DMS	0.1030	0.0896	0.1329	0.0917	0.0375	0.0465	0.0965	0.0549
DMDS	0.4028	0.5825	0.4210	0.1419	0.4466	0.7195	0.7879	0.3558

0.8 g **TIME (hrs)**

	0	3	6	9	12	15	18	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0144	0.0182	0.0165	0.0292	0.0264	0.0200	0.0781	0.0172
CDS	0.0013	0.0010	0.0009	0.0010	0.0010	0.0010	0.0011	0.0009
DMS	0.0104	0.0093	0.0118	0.0566	0.0385	0.0188	0.0860	0.0058
DMDS	0.0048	0.0477	0.0948	0.3441	0.2963	0.4568	1.1185	0.4901

pH **TIME (hrs)**

Sample	**0**	**3**	**6**	**9**	**12**	**15**	**18**	**24**
control	7.10	7.12	7.42	7.27	7.13	6.91	6.96	7.34
0.3 g	7.62	7.68	7.61	7.47	7.51	7.20	7.34	7.47
0.5 g	7.58	7.64	7.68	7.49	7.57	7.40	7.42	7.53
0.8 g	7.57	7.77	7.98	7.77	7.67	7.62	7.57	7.66

ORP **TIME (hrs)**

Sample	**0**	**3**	**6**	**9**	**12**	**15**	**18**	**24**
control	-244.5	-248.5	-230.6	-230.6	-229.4	-223.6	-216.2	-211.3
0.3 g	-226.7	-267.7	-256.4	-256.6	-256.6	-254.7	-201.4	-232.2
0.5 g	-139.1	-204.4	-213.8	-208.9	-206.1	-221.8	-224.2	-237.7
0.8 g	-89.8	-156.4	-156.4	-196.4	-207.0	-216.4	-238.6	-248.3

Potassium Permangante (Gravity) oxidation results

CONTROL **TIME (hrs)**

	0	3	6	9	12	15	21	24
Compound	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0173	0.0179	0.0185	0.0149	0.0160	0.0160	0.0154	0.0148
CDS	0.0011	0.0011	0.0012	0.0013	0.0011	0.0010	0.0011	0.0009
DMS	0.0265	0.0012	0.0038	0.0020	0.0006	0.0003	0.0007	0.0004
DMDS	0.0175	0.0075	0.0164	0.0040	0.0130	0.0030	0.0042	0.0024

0.3 g **TIME (hrs)**

	0	3	6	9	12	15	21	24
Compound	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0140	0.0150	0.0171	0.0174	0.0196	0.0204	0.0153	0.0158
CDS	0.0018	0.0011	0.0013	0.0012	0.0009	0.0011	0.0020	0.0009
DMS	0.0008	0.0008	0.0023	0.0024	0.0004	0.0011	0.0015	0.0009
DMDS	0.0001	0.0007	0.0066	0.0141	0.0112	0.0260	0.0077	0.0052

0.5 g **TIME (hrs)**

	0	3	6	9	12	15	21	24
Compound	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0143	0.0150	0.0143	0.0138	0.0142	0.0147	0.0150	0.0144
CDS	0.0017	0.0014	0.0018	0.0016	0.0012	0.0012	0.0012	0.0009
DMS	0.0008	0.0007	0.0013	0.0002	0.0001	0.0002	0.0007	0.0004
DMDS	0.0001	0.0002	0.0001	0	0.0001	0.0004	0.0008	0.0005

0.8 g **TIME (hrs)**

	0	3	6	9	12	15	21	24
C ompound	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0141	0.0146	0.0143	0.0137	0.0145	0.0143	0.0139	0.0137
CDS	0.0013	0.0010	0.0012	0.0011	0.0010	0.0010	0.0012	0.0009
DMS	0.0020	0.0003	0.0012	0.0004	0.0003	0.0001	0.0003	0.0002
DMDS	0.0001	0.0001	0.0001	0.0000	0.0001	0.0001	0.0002	0.0001

pH **TIME (hrs)**

Sample	**0**	**3**	**6**	**9**	**12**	**15**	**21**	**24**
control	na	6.11	6.12	6.12	6.22	6.31	6.37	6.49
0.3 g	na	7.08	7.26	7.23	7.15	7.12	7.19	7.14
0.5 g	na	7.20	7.30	7.24	7.20	7.16	7.27	7.18
0.8 g	na	7.57	7.41	7.41	7.23	7.08	7.03	7.06

ORP **TIME (hrs)**

Sample	**0**	**3**	**6**	**9**	**12**	**15**	**21**	**24**
control	-135.0	-101.6	-78.7	-84.1	-68.9	-72.7	-65.1	-83.6
0.3 g	82.8	-129.2	-158.4	-154.3	-145.0	-134.4	-146.0	-133.3
0.5 g	220.2	162.8	70.5	-3.3	-61.8	-61.8	-155.3	-150.1
0.8 g	-20.8	351.5	330.5	304.1	290.7	272.5	256.1	201.4

Sodium Hypochlorite (DAF) oxidation results

CONTROL **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0189	0.0227	0.0434	0.0427	0.0245	0.0291
CDS	0.0010	0.0009	0.0009	0.0009	0.0009	0.0009
DMS	0.2115	0.0784	0.0829	0.0753	0.0256	0.0461
DMDS	0.0256	0.0468	0.2766	0.3192	0.0761	0.0703

0.3 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0915	0.0291	0.0496	0.0418	0.0261	0.0229
CDS	0.0011	0.0010	0.0009	0.0009	0.0009	0.0009
DMS	0.1449	0.0576	0.0736	0.0312	0.0186	0.0190
DMDS	0.1919	0.3335	0.4361	0.2843	0.0758	0.0276

0.5 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0239	0.0826	0.0384	0.0431	0.0246	0.0228
CDS	0.0011	0.0009	0.0009	0.0008	0.0009	0.0009
DMS	0.0465	0.4357	0.0920	0.0351	0.0521	0.0466
DMDS	0.1619	0.6103	0.5149	0.1812	0.1558	0.0737

0.8 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	Ppmv	ppmv	ppmv	ppmv
MM	0.0212	0.0380	0.0432	0.0621	0.0259	0.0253
CDS	0.0014	0.0010	0.0009	0.0009	0.0008	0.0009
DMS	0.0418	0.0682	0.2478	0.0388	0.0186	0.0234
DMDS	0.1820	0.5654	0.7741	0.1749	0.0559	0.0666

pH **TIME (hrs)**

Sample	0	4	8	12	20	24
Control	6.93	6.94	6.97	6.78	6.70	6.67
0.3 g	6.97	6.98	6.83	6.77	6.62	6.57
0.5 g	6.98	6.97	6.86	6.76	6.60	6.55
0.8 g	6.98	6.97	6.84	6.76	6.65	6.57

ORP **TIME (hrs)**

Sample	0	4	8	12	20	24
Control	-228.6	-235.4	-220.9	-201.5	-167.1	-153.8
0.3 g	-204.9	-214.6	-198.3	-167.9	-134.7	-126.9
0.5 g	-180.2	-226.5	-191.7	-162.8	-127.8	-129.2
0.8 g	-217.3	-193.5	-186.6	-176.3	-115.2	-121.6

Sodium Hypochlorite (GR) oxidation results

CONTROL **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0175	0.0188	0.0183	0.0155	0.0169	0.0176
CDS	0.0014	0.0010	0.0009	0.0009	0.0008	0.0010
DMS	0.2882	0.0089	0.0010	0.0004	0.0012	0.0009
DMDS	0.0048	0.0038	0.0009	0.0012	0.0019	0.0051

0.3 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0174	0.0162	0.0163	0.0151	0.0147	0.0153
CDS	0.0010	0.0009	0.0009	0.0009	0.0009	0.0010
DMS	0.0194	0.1221	0.0263	0.0190	0.0113	0.0117
DMDS	0.0011	0.0010	0.0008	0.0008	0.0007	0.0010

0.5 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0172	0.0200	0.0206	0.0147	0.0148	0.0154
CDS	0.0011	0.0009	0.0009	0.0009	0.0009	0.0009
DMS	0.0536	0.0973	0.0240	0.0078	0.0159	0.0087
DMDS	0.0017	0.0022	0.0007	0.0011	0.0003	0.0006

0.8 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0163	0.0159	0.0151	0.0156	0.0148	0.0151
CDS	0.0011	0.0010	0.0009	0.0009	0.0009	0.0010
DMS	0.0103	0.0218	0.0835	0.0080	0.0090	0.0298
DMDS	0.0006	0.0009	0.0006	0.0007	0.0003	0.0046

pH **Time (hrs)**

Sample	0	4	8	12	20	24
Control	5.83	5.79	6.02	6.02	6.34	6.16
0.3 g	5.83	5.85	6.04	6.12	6.25	6.34
0.5 g	5.87	5.90	6.11	6.09	6.16	6.39
0.8 g	5.97	6.00	6.13	6.14	6.40	6.43

ORP **Time (hrs)**

Sample	0	4	8	12	20	24
Control	-148.1	-95.9	-29.6	-72.5	-48.5	-43.1
0.3 g	-139.3	-106.0	-93.6	-62.7	-27.1	-60.3
0.5 g	-90.8	-64.9	-72.5	-34.4	-26.4	-60.4
0.8 g	-89.2	-61.1	-32.9	-39.3	-72.3	-103.4

Calcium Nitrate (DAF) oxidation results

CONTROL **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0344	0.0500	0.0751	0.0662	0.0201	0.0214
CDS	0.0017	0.0019	0.0021	0.0015	0.0013	0.0012
DMS	0.1498	0.0483	0.0902	0.0161	0.0134	0.0150
PM	0.0153	0.0120	0.0110	0.0103	0.0000	0.0000
DMDS	0.4669	0.6048	0.3761	0.2429	0.1200	0.0354

0.3 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0148	0.0396	0.0366	0.0872	0.0256	0.0293
CDS	0.0009	0.0015	0.0019	0.0019	0.0015	0.0013
DMS	0.0437	0.0146	0.0190	0.0493	0.0171	0.0111
PM	0.0125	0.0103	0.0000	0.0107	0.0000	0.0102
DMDS	0.0051	0.2245	0.3513	0.5670	0.2120	0.0574

0.5 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0139	0.0230	0.0650	0.0700	0.0327	0.0299
CDS	0.0010	0.0014	0.0014	0.0015	0.0020	0.0012
DMS	0.0169	0.0064	0.0453	0.0178	0.0186	0.0094
PM	0.0000	0.0105	0.0000	0.0000	0.0000	0.0101
DMDS	0.0002	0.0543	0.1647	0.1980	0.3015	0.0968

0.8 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0135	0.0141	0.0140	0.0154	0.0298	0.0382
CDS	0.0011	0.0010	0.0009	0.0010	0.0023	0.0022
DMS	0.0061	0.0024	0.0006	0.0007	0.0031	0.0034
PM	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMDS	0.0003	0.0017	0.0023	0.0059	0.4867	0.7250

pH **Time (hrs)**

Sample	0	4	8	12	20	24
Control	7.15	7.29	7.21	7.26	7.14	7.06
0.3 g	7.29	7.43	7.36	7.37	7.28	7.20
0.5 g	7.13	7.48	7.37	7.45	7.35	7.29
0.8 g	6.99	7.63	7.31	7.57	7.47	7.49

ORP **Time (hrs)**

Sample	0	4	8	12	20	24
Control	-228.9	-213.1	-197.7	-212.5	-163.7	-171.4
0.3 g	-217.2	-252.5	-225.8	-211.6	-198.5	-186.1
0.5 g	-216.6	-242.1	-219.9	-206.7	-185.0	-188.2
0.8 g	-182.0	-80.0	-130.4	-125.9	-147.8	-129.9

Calcium Nitrate (GR) oxidation results

CONTROL **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0185	0.0166	0.0174	0.0180	0.0350	0.0341
CDS	0.0020	0.0022	0.0016	0.0018	0.0010	0.0010
DMS	0.1253	0.0002	0.0002	0.0003	0.0007	0.0009
DMDS	0.0013	0.0013	0.0020	0.0061	0.0340	0.0717

0.3 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0177	0.0151	0.0162	0.0154	0.0264	0.0208
CDS	0.0021	0.0020	0.0012	0.0015	0.0010	0.0010
DMS	0.1209	0.0001	0.0000	0.0002	0.0000	0.0000
DMDS	0.0013	0.0007	0.0004	0.0011	0.0261	0.0146

0.5 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0163	0.0150	0.0155	0.0154	0.0160	0.0155
CDS	0.0019	0.0015	0.0013	0.0014	0.0012	0.0012
DMS	0.0637	0.0001	0.0000	0.0001	0.0000	0.0000
DMDS	0.0005	0.0002	0.0005	0.0005	0.0022	0.0018

0.8 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0147	0.0152	0.0157	0.0149	0.0149	0.0152
CDS	0.0014	0.0020	0.0016	0.0010	0.0010	0.0010
DMS	0.0230	0.0000	0.0000	0.0000	0.0000	0.0000
DMDS	0.0002	0.0004	0.0003	0.0006	0.0006	0.0017

pH **Time (hrs)**

Sample	0	4	8	12	20	24
Control	5.74	5.70	5.80	5.84	6.01	6.09
0.3 g	5.76	5.96	6.17	6.32	6.63	6.84
0.5 g	5.78	6.02	6.14	6.23	6.66	7.14
0.8 g	5.69	5.95	6.16	6.17	6.45	6.84

ORP **Time (hrs)**

Sample	0	4	8	12	20	24
Control	-77.4	-60.8	-37.9	-27.3	-47.4	-35.0
0.3 g	-101.6	-90.3	-70.7	-66.1	-92.7	-83.8
0.5 g	-96.5	-80.7	-69.7	-59.5	-67.8	-82.0
0.8 g	-108.7	-90.7	-69.9	-71.1	-71.3	-87.8

Potassium Ferrate (DAF) oxidation results

CONTROL **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0199	0.1008	0.0747	0.0937	0.1308	0.0815
CDS	0.0010	0.0015	0.0012	0.0011	0.0011	0.0010
DMS	0.0127	0.1505	0.2464	0.2206	0.5255	0.3811
DMDS	0.0087	0.4811	0.4808	0.8146	0.9520	0.6409

0.3 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0424	0.1007	0.1523	0.1353	0.2694	0.0363
CDS	0.0014	0.0012	0.0012	0.0010	0.0009	0.0012
DMS	0.0769	0.0852	0.0479	0.0279	0.1575	0.0506
DMDS	0.6454	0.4399	0.4429	0.2846	0.1944	0.1886

0.5 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.1269	0.0957	0.1031	0.1088	0.0910	0.0577
CDS	0.0015	0.0013	0.0014	0.0014	0.0014	0.0011
DMS	0.2770	0.0511	0.0680	0.0363	0.0402	0.0420
DMDS	1.3088	0.7255	1.0471	1.1560	0.5143	0.2796

0.8 g **TIME (hrs)**

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0362	0.0790	0.0790	0.0943	0.1176	0.0930
CDS	0.0015	0.0013	0.0012	0.0011	0.0010	0.0010
DMS	0.0257	0.0693	0.0810	0.0266	0.0215	0.0757
DMDS	0.3360	0.5956	0.8562	0.7648	1.0300	0.8184

pH **Time (hrs)**

Sample	0	4	8	12	20	24
Control	6.90	6.85	7.03	6.89	6.98	7.04
0.3 g	7.19	7.31	7.21	7.15	6.97	7.01
0.5 g	7.39	7.28	7.29	7.26	7.15	7.14
0.8 g	7.66	7.39	7.36	7.36	7.30	7.31

ORP **Time (hrs)**

Sample	0	4	8	12	20	24
Control	-215.6	-237.5	-223.2	-231.8	-230.8	-227.6
0.3 g	-227.2	-247.5	-223.2	-211.3	-189.3	-174.0
0.5 g	-197.7	-218.5	-208.2	-201.1	-179.0	-174.7
0.8 g	-196.2	-228.8	-219.8	-218.6	-211.8	-200.5

Potassium Ferrate (GR) oxidation results

CONTROL

TIME (hrs)

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0158	0.0159	0.0154	0.0152	0.0135	0.0147
CDS	0.0010	0.0017	0.0013	0.0012	0.0012	0.0010
DMS	0.3630	0.0036	0.0004	0.0003	0.0003	0.0000
DMDS	0.0011	0.0029	0.0018	0.0015	0.0011	0.0005

0.3 g

TIME (hrs)

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0158	0.0170	0.0179	0.0347	0.0169	0.0165
CDS	0.0013	0.0016	0.0015	0.0017	0.0011	0.0020
DMS	0.0404	0.0028	0.0004	0.0010	0.0004	0.0012
DMDS	0.0010	0.0050	0.0147	0.0234	0.0043	0.0143

0.5 g

TIME (hrs)

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0152	0.0146	0.0163	0.0236	0.0215	0.0229
CDS	0.0011	0.0015	0.0013	0.0012	0.0012	0.0018
DMS	0.0788	0.0095	0.0009	0.0007	0.0007	0.0030
DMDS	0.0009	0.0005	0.0028	0.0273	0.0176	0.0223

0.8 g

TIME (hrs)

	0	4	8	12	20	24
Chemical	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
MM	0.0329	0.0141	0.0155	0.0325	0.0231	0.0367
CDS	0.0013	0.0010	0.0013	0.0019	0.0011	0.0010
DMS	0.0065	0.0012	0.0018	0.0045	0.0017	0.0061
DMDS	0.0002	0.0000	0.0028	0.0859	0.0239	0.0100

pH

Time (hrs)

Sample	0	4	8	12	20	24
Control	5.63	5.61	5.65	5.80	5.75	5.73
0.3 g	6.41	6.57	6.53	6.59	6.86	6.93
0.5 g	6.64	6.96	6.94	6.96	7.12	7.18
0.8 g	6.97	7.36	7.38	7.42	7.51	7.53

ORP

Time (hrs)

Sample	0	4	8	12	20	24
Control	-129.5	-167.8	-135.6	-127.0	-16.7	-19.6
0.3 g	-122.3	-147.0	-148.1	-133.0	-132.5	-146.6
0.5 g	-102.7	-141.3	-172.3	-160.5	-156.0	-155.5
0.8 g	-117.8	-116.4	-154.0	-151.0	-143.2	-111.0

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